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Principles of Vacuum Engineering

PRINCIPLES OF VACUUM ENGINEERING

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Introduction

Almost all the principal engineering disciplines which contribute to contemporary amenities constitute the last of three development phases—pure research, exploring and establishing the basic phenomena; applied research, giving experimental proof of the practical potentialities; and engineering design, applying the results to conditions in practice. Vacuum engineering is no exception but, compared with other branches of engineering, it is still young. The establishment of organized vacuum engineering activity is generally recognized to have coincided with the development of the atomic energy project in the last war. Ever since, the uses of vacuum engineering have expanded with the speed so characteristic of post-war and present-day technological development.

Basically vacuum engineering is concerned with apparatus for the production and maintenance of a vacuum and with instruments for the measurement of sub-atmospheric pressures. Thus, vacuum plant is essentially a tool. A tool will perform satisfactorily only if the designer is familiar with the characteristics of the process for which the tool is to be employed and if the user is familiar with the characteristics of the tool mechanism. This may sound a truism, but has particular significance in this sphere, where extension of vacuum methods to new fields more often than not presents problems genuinely lacking an immediate answer and calling for an exceptional depth of knowledge in both directions to find a solution.

The broad knowledge required to exploit vacuum techniques in all the potential fields of application is hardly ever to be found in any one person or even in one organization. This situation is strongly reflected in the available vacuum literature. There is only one author who has provided truly comprehensive information on the subject—S. Dushman in his magnificent reference work *Scientific Foundations of Vacuum Technique*, now regarded as a classic. This book, essentially a dossier of results achieved in work at the applied research level, ended a period of book publishing on vacuum, never resumed since on a noticeable scale. Progress during the past ten years has mainly been reported in the form of contributions to journals, with the attendant restriction in scope. In particular, no attempt has been made to give an all-embracing account of recent advances at the engineering level.

Since these advances are considerable, the present publishers feel that the time is appropriate to compile and present a comprehensive record of the development of vacuum engineering, methodically planned to cover as many specialized applications as possible. To ensure flexibility of approach, a series of monographs will be published, each volume concentrating on a particular subject. The texts are conceived with a view to assisting the operator rather than the maker of equipment, and both the design engineer and the specialised user will report in this series.

As publication proceeds, therefore, information will be produced which will profitably extend the knowledge of both designer and user, and it is hoped that these monographs may materially assist in promoting the art in this way.

H. L. J. Burgess

Preface

The number of published papers on vacuum technology and its applications is so vast that it is impossible to write a comprehensive survey in a single volume. Nevertheless, our attempt in the present book would seem to be justified for three main reasons: firstly, there have been many new advances in the past ten years; secondly, little has been included in previous books on the application of vacuum technology; thirdly, selection from the immense store of published information is necessary to try to assess its importance and to direct the overburdened reader. In the selection of material, guiding principles have been to give descriptions of most of the basic apparatus and techniques, to include especially data of practical value, and to give weight to those methods and practices of which the authors have direct experience. In this last context, it has sometimes been preferred to give a detailed description of one well-tried technique or application rather than attempt to discuss all possibilities.

Theoretical explanations given in the text tend to be brief, partly because only that theory substantially of use in practical work is included, partly because it is felt that excessive theory is sometimes not too helpful to the technologist faced with given apparatus, usually provided by a manufacturer.

In order to atone for our many sins of omission, an extensive but carefully selected bibliography is given which is referred directly to the text and where the full titles of the papers are noted to enable an apt choice of further reading to be made.

Moreover, a list of manufacturers of equipment is included because not all details of an item can be discussed in this text and because it is undoubtedly true that most vacuum technicians have frequently to contact the specialist in the supply industry for information. If, as is unfortunately likely, manufacturers have been overlooked, apologies are offered in advance. The omission is due to lack of knowledge which will be rectified in any future edition if the organisation concerned cares to write to the authors.

Grateful thanks are due to many individuals and firms who have supplied information, diagrams and photographs. It is hoped that sufficient recognition of these services is given in the text. Especial acknowledgements for assistance are due to Mrs. J. Bangert and Miss P. Siggs for typing the manuscript, to Mr. A. C. Ashley, chief laboratory steward at The Polytechnic, Regent Street, W.1., for data on many practical matters, and to Mrs. D. Yarwood who drew many of the diagrams.

M. PIRANI
J. YARWOOD

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Note

Throughout this text the unit of pressure employed is the *torr*.
1 torr = 1 mm of mercury (mm Hg) within 1 part in 7×10^6. (*see* British Standard 2951:1958, *Glossary of Terms Used in High Vacuum Technology*, British Standards Institution, London).
760 torr = 1 standard atmosphere (atm); 1 millitorr = 10^{-3} torr = 1 micron

1

VACUUM SYSTEMS

Definitions, Graphs, Charts and Formulae

1.1. Types of System

Vacuum systems may be conveniently classified into two types: **static systems** and **kinetic systems.** A static system is defined as one in which there is little appreciable continuous evolution of gas, *i.e.* the air leaks are very small and the out-gassing of the components of, and the materials in, the system is small. By small is meant, more precisely, that the rate of evolution of gas is insignificant compared with the effective speed of the pump or combination of pumps used. A kinetic system, on the other hand, is one in which there is an appreciable evolution of gas into the system during pumping, such evolution being due to either leaks from the atmosphere or considerable outgassing of materials of, or in, the system. The chief example of a static system is the pumping of an air-tight glass vessel, *e.g.* an electron tube, whilst an example of a kinetic system is a demountable apparatus for the evaporation of metals *in vacuo* (§ 10.5).

There is no sharp dividing line between static and kinetic. Indeed, a nominally static system may, in certain circumstances, become a kinetic one during a pumping schedule. For example, a thermionic vacuum tube on a mercury diffusion pump/backing pump combination is a static system; yet if the electrodes of the tube are rapidly degassed by eddy-current heating, kinetic considerations apply. Despite a lack of definite distinction between the use of the terms 'static' and 'kinetic', these classifications are convenient because, in general, the flow of gas through a static system is so small that the speed of pumping is usually—and indeed often necessarily—a minor consideration compared with the ultimate vacuum achievable, whereas in the kinetic system, considerable gas flow, demanding high pumping speed and hence the consideration of short, wide connecting tubes (§ 1.4), is one of the major design requirements.

Vacuum systems might also be classified as small and large systems. If the vessel to be evacuated—hereafter called the **vacuum tank**—has a volume of 10 litres or more, it might be said to be large. The distinction is, however, somewhat arbitrary, though a large system will almost always be of the kinetic type.

A small static or kinetic system will comprise the following main items:

(*a*) a **mechanical rotary pump** used as a **backing pump**, *i.e.* **fore-pump**;

(*b*) a **diffusion pump** or **ion pump** if an ultimate pressure of less than 10^{-} torr is required, and especially if considerable gas evolution at this and lower pressures is encountered;

(*c*) a **cold trap** or **baffle**;

(*d*) the vacuum tank;

(*e*) a **vacuum gauge**; in some cases, two gauges are desirable, one connected to the backing pump and the other to the vacuum tank.

The rotary pump is connected in series with, or 'backs' the diffusion pump. The rotary pump operates relative to atmospheric pressure; the diffusion pump requires a backing pressure of the order of 0·1 to 0·5 torr.

These basic requirements are illustrated in Fig. 1.1(*a*). Here a small static glass system with a mercury diffusion pump is shown; a glass or welded steel reservoir of volume about 5 litres inserted between the backing pump and the diffusion pump enables the rotary backing pump to be isolated by the valve V_1, once the necessary backing pressure has been established. This provision is often a convenience in small-scale experimental work as the noise and vibration of the rotary pump are avoided during most of the operating time. Using such a static system, the pressure in the vacuum tank—the so-called **fine-side** or **inlet side** pressure—can readily be reduced to 10^{-6} torr.

A large kinetic system (Fig. 1.1(*b*)) comprises the same basic items. If very considerable gas evolution is encountered, it is usually good practice, but dependent upon the circumstances, to incorporate an **ejector pump** (§ 2.18) (also known as a **booster pump**) between the diffusion and mechanical rotary pumps. This ejector is often an integral part of a **diffusion-ejector pump** (as in Fig. 1.1(*b*)). Alternatively, a **Roots pump** (§ 2.7) is placed between the mechanical rotary pump and the diffusion pump. If pressures below 10^{-4} torr are not required and high pumping speed is necessary in the pressure range from 10^{-1} to 10^{-3} torr, an ejector or a Roots pump backed by a rotary pump is used without the diffusion pump.

A small mechanical rotary pump used as a **holding pump** is often valuable on large kinetic systems; another useful arrangement is a **by-pass line**. These are both shown in Fig. 1.1(*b*). To operate such a system, the air-inlet valve AV_1 (Fig. 1.1(*c*)) and the isolation valves (*see* Chapter 5) V_1 and V_3 are closed, the large **gas-ballast pump** (§ 2.5) is switched on and valve V_2 is opened. The vacuum tank is thereby exhausted to a pressure of about 10^{-1} torr (*i.e.* it is 'roughed out'). Meanwhile, the air-inlet valve AV_2 is closed and the isolation valve V_4 opened and the small rotary holding pump started. The latter exhausts the diffusion-ejector pump to a pressure low enough to enable the pump heater to be switched on. After the vacuum tank has been roughed out and the diffusion-ejector pump has warmed up, valves V_2 and V_4 are closed and V_3 and V_1 opened. The pressure in the vacuum tank is then reduced to 10^{-5} torr or less. If, subsequently, the gas evolution from the tank is small, the valve V_3 may be closed, V_4 opened and the necessary backing pressure maintained by the small holding pump alone.

A by-pass line with suitable valves or stopcocks can also be used on a static or small kinetic system but the holding pump is then not necessary, provided the leak rate into the backing space (best provided with a reservoir) is negligible. The provision of a by-pass line in both cases enables the diffusion pump to be kept hot and under vacuum through a series of vacuum operations, in between which air is let into the rest of the system.

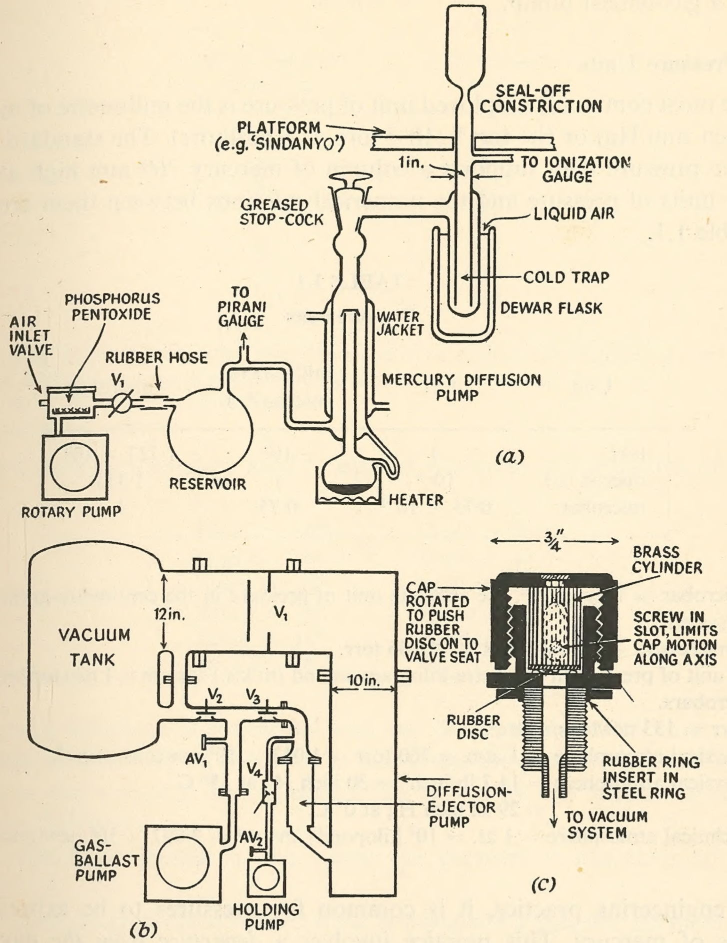
SEAL-OFF CONSTRICTION
PLATFORM (e.g.'SINDANYO')
1in.
TO IONIZATION GAUGE
GREASED STOP-COCK
LIQUID AIR
COLD TRAP
DEWAR FLASK
PHOSPHORUS PENTOXIDE
TO PIRANI GAUGE
AIR INLET VALVE
WATER JACKET
RUBBER HOSE
V_1
MERCURY DIFFUSION PUMP
(*a*)
RESERVOIR
ROTARY PUMP
HEATER
3/4"
BRASS CYLINDER
12in.
V_1
VACUUM TANK
CAP ROTATED TO PUSH RUBBER DISC ON TO VALVE SEAT
SCREW IN SLOT, LIMITS CAP MOTION ALONG AXIS
10in.
V_2
V_3
RUBBER DISC
AV_1
V_4
RUBBER RING INSERT IN STEEL RING
DIFFUSION-EJECTOR PUMP
TO VACUUM SYSTEM
GAS-BALLAST PUMP
AV_2
HOLDING PUMP
(*b*)
(*c*)

FIG. 1.1
(*a*) A small static vacuum system
(*b*) A large kinetic vacuum system
(*c*) An air-inlet valve

As an alternative to an air-inlet valve, a stopcock may be used or, in the case of small glass systems, a glass seal-off pip which can be readily snapped and re-fused by a blow-pipe.

A **phosphorus pentoxide trap** is often used between the rotary backing pump and the diffusion pump to absorb water vapour (Fig. 1.1(*a*)). If, however, a gas ballast pump is used for backing, the phosphorus pentoxide trap is often unnecessary. Whereas the normal mechanical rotary (or piston) pump will not cope with any considerable evolution of water vapour (§ 2.4) the gas ballast pump will do so. Gas ballast pumps are almost invariably used on large kinetic systems; nevertheless precautions against water and other vapours are often necessary, depending on the circumstances prevailing. It is not necessarily good practice to discard the phosphorus pentoxide trap when using a gas-ballast pump.

1.2. Pressure Units

The most commonly employed unit of pressure is the millimetre of mercury (written mm.Hg) or the **torr**[*] (10^{-3} torr = 1 millitorr). The standard atmospheric pressure then supports a column of mercury 760 mm high at 0° C. Other units of pressure and the numerical relations between them are given in Table 1.1.

TABLE 1.1

Pressure units

Unit	torr	millitorr or micron (μ)	microbar
torr	1	10^3	$1{\cdot}333 \times 10^3$
micron (μ)	10^{-3}	1	1·333
microbar	$0{\cdot}75 \times 10^{-3}$	0·75	1

1 microbar ≡ 1 dyne/cm^2, the absolute unit of pressure in the centimetre-gram-second (c.g.s) system.

10^6 microbars ≡ 10^3 millibars ≡ 750·06 torr.

The unit of pressure in the metre-kilogram-second (m.k.s.) system is 1 newton/metre^2 ≡ 10 microbars.

1 torr = 133 newtons/metre^2.

1 physical atmosphere = 1 atm = 760 torr = $1{\cdot}013 \times 10^5$ newtons/metre^2.

1 physical atmosphere = 14·7 lb/inch^2 = 30 inch Hg at 15° C
= 29·92 inch Hg at 0° C.

1 technical atmosphere = 1 at. = 10^4 kilopond[†]/metre^2 = $9{\cdot}807 \times 10^4$ newtons/metre^2.

In engineering practice, it is common for pressures to be expressed in inches of mercury. This practice involves a *departure from the physicist's usual conception of pressure measurement*. Thus, the engineering practice regards 30 *inch Hg as a high vacuum*, and not as atmospheric pressure. This practice arises from the fact that a pump capable of producing a good vacuum would produce a rise of 30 inches in a simple mercury manometer to which it was connected, whereas the physicist's concept is concerned with the height of the mercury column which would be balanced against the given pressure.

Since the height of the barometer depends on atmospheric pressure and

---

[*] The adoption of the term 'torr' in place of 'mm of mercury' is recommended by the British Standards Institution and the American French and German Vacuum Societies.

[†] The kilopond ≡ kilogram weight.

temperature conditions, this engineering practice is only suitable for the specification of rough vacua.

Table 1.2 may be therefore compiled.

1 inch = 25·4 mm

TABLE 1.2

Engineering scale inches Hg	Physics scale torr
30[1]	0
29[2]	25·4
20	254
15	381
10	508
5	635
0[3]	760

[1] A perfect vacuum, but cannot really be specified on such a scale because the atmospheric pressure and temperature prevailing would also have to be stated.

[2] *i.e.* 30 − 29 = 1 inch off perfect.

[3] Atmospheric pressure.

The following terms are used to express multiples and fractions of unity:

Tera T:	10^{12}	Deci d:	10^{-1}
Giga G:	10^9	Centi c:	10^{-2}
Mega M:	10^6	Milli m:	10^{-3}
Kilo K:	10^3	Micro μ:	10^{-6}
Hecto H:	10^2	Nano n:	10^{-9}
Deca D:	10	Pico p:	10^{-12}

Vacuum technique is concerned with any pressure below 760 torr.

A **high vacuum** may be classified as one where the pressure is less than 10^{-3} torr (*i.e.* one micron). This classification is not by any means universally adopted, however.

An **ultra-high vacuum** is one where the pressure is less than 10^{-7} torr (≡ 10^{-4} μ).

The term **rough vacuum** is often used to designate a pressure between 1 torr and 760 torr, whilst the range from 10^{-3} to 1 torr may be called a **medium vacuum.**

1.3. Pump Speed

The speed of a vacuum pump of any type is defined according to Gaede. The speed S of a pump at a pressure p is the volume of gas removed from the system per unit of time, where this volume is measured at the pressure p.

It is important to emphasize that pump speed defined in this manner is a function of the pressure prevailing at the pump inlet. This function is not a simple mathematical one. Indeed, the speed of pumps is constant over reasonably wide ranges, but falls off at pressures, and in a manner, depending on a number of considerations (Chapter 2).

The determination of pump speed in accordance with this definition implies that a vessel of infinite volume is being pumped. Otherwise, the pressure in the vessel will decrease during pumping. In practical determinations of pump speed, an infinite volume is simulated by an adjusted rate of leak of air or gas into the vessel used. The constant equilibrium pressure attained depends on the leak rate balanced against the speed of pumping. A needle valve (§ 5.17) is usually employed for such adjustable leaks.*

The units of pumping speed employed in most of this text are (*a*) the litre/minute for mechanical rotary pumps (*b*) the litre/second for diffusion and other vapour stream pumps. Other units are often employed. The relationships between them are given in Table 1.3.

TABLE 1.3
Units of pump speed

Unit	cu cm/sec	litre/sec	litre/min	cu metre/hour	cu ft/min
cu cm/sec	1	0·001	0·060	0·0036	0·0021
litre/sec	1000	1	60	3·6	2·12
litre/min	16·67	0·0167	1	0·060	0·0353
cu metre/hour	277·8	0·2778	16·67	1	0·589
cu ft/min	471·95	0·4719	28·32	1·699	1

Note: 1 cu ft = 28·316 litres
1 litre = 0·035316 cu ft.

Despite the frequent usage of one or other of the above units of pump speed, it is often preferable to measure gas flow into the pump in grams of gas per second (§ 2.17).

1.4. Impedance and Conductance

It is imperative to realize that the effective speed of pumping at the vacuum tank is almost always less than, and often considerably less than, the speed of the pump as determined by experiment or given in the manufacturers' catalogues. This is because of the impedance to gas flow of the connecting tubing, valves, traps, baffles, etc., between the pump and the tank. *This tubing should be as short and wide as possible*, especially in the case of large, kinetic vacuum systems (*see* § 1.5).

If, at any point in the vacuum circuit, defined as the series combination of rotary pump, tubing, diffusion pump, traps and valves (if used) and tank, a cross-section plane is considered, then, if V is the volume of gas flowing across this plane per unit time and p is the pressure at that plane,

$$Q = pV \tag{1.1}$$

defines Q, the gas flow traversing that plane. This gas flow is known as the **throughput.**

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* For methods of measuring pump speed, *see* Dushman, D1; Jaeckel, J1; Yarwood, Y1; Oatley, O1; Rufer, R1.

By Boyle's law, pV is a constant for a given mass of perfect gas at a given temperature. For all but the condensable vapours (defined as those gases which are liquefied at room temperature or above by application of pressure alone) the gases encountered at low pressures can be considered as perfect gases. Hence, the throughput Q must be the same at all points in the circuit. Thus, there cannot be an accumulation of gas at any point in the system whilst gas flow to the pump and out to the atmosphere takes place.

Equation (1.1) may be extended by writing

$$Q = pV = \mathbf{k}nT \tag{1.2}$$

where **k** is Boltzmann's constant (*see* Appendix A), T is the absolute temperature and n is the number of molecules crossing the plane per unit time. Multiplying by m, the mass of the gas molecule, it follows that the mass of gas flowing per unit time past all cross-section planes in the vacuum circuit is constant. This is, of course, an expected result. The flow in gram/sec is known as the **mass-throughput.**

Q is usually given in the units of litres per second at a pressure of one torr at 20° C, *i.e.* litre torr per sec (*see* also § 9.3).

The **impedance** Z (sometimes called the **resistance**) of any part of the vacuum circuit, *e.g.* a length of pipe in the circuit, is then defined as the pressure difference per unit throughput; therefore:

$$Z = \frac{p_1 - p_2}{Q} \tag{1.3}$$

where p_1 and p_2 are the pressures at the high and low sides respectively of the element of the vacuum circuit concerned.

The **conductance** U of an orifice, tube or duct is the reciprocal of the impedance, therefore:

$$U = \frac{1}{Z} = \frac{Q}{p_1 - p_2} \tag{1.4}$$

The conductance is given in litre/sec, or in any other of the units given in Table 1.3. The unit of impedance is hence the sec/litre. Though conductance and pump speed (§ 1.3) have the same units, the terms have different meanings because the use of the term 'pump speed' implies an external source of power.

If a number of tubes or ducts of any type, including valves, traps, etc., 1, 2, 3, 4 . . ., have, respectively, conductances U_1, U_2, U_3, U_4 . . ., then:

For conductances in parallel

$$U = U_1 + U_2 + U_3 + U_4 + \tag{1.5}$$

where U is the resultant conductance. Hence

$$\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3} + \frac{1}{Z_4} + \tag{1.6}$$

where Z is the resultant impedance and Z_1, Z_2, Z_3, Z_4 . . . are the individual impedances.

For **conductances in series***

$$\frac{1}{U} = \frac{1}{U_1} + \frac{1}{U_2} + \frac{1}{U_3} + \frac{1}{U_4} + \qquad (1.7)$$

and for the corresponding impedances

$$Z = Z_1 + Z_2 + Z_3 + Z_4 + \qquad (1.8)$$

1.5. Formulae, Graphs and Abacs Concerned with Conductances

The theory and formulae relevant depend on the order of pressure prevailing. If, in the case of flow through a single aperture, the mean free path λ of the gas (*see* Appendix A) is greater than the linear dimensions of the aperture, then **molecular effusion** prevails. For flow through a tube, where λ is greater than the inside dimensions of the cross-section of the tube, **molecular flow** prevails. In these two cases, collisions of the molecules with the walls of the aperture or pipe are responsible for the impedance to gas flow. Collisions of the molecules with one another are comparatively insignificant in their effect.

If, in flow through pipes, the mean free path of the gas molecules is very small compared with the inside dimensions of the pipe, then inter-molecular collisions are much more important than collisions of the molecules with the walls. The transport of the gas through the tube is then described as **viscous flow.** At still higher gas pressures and velocities, the flow becomes **turbulent**. Turbulence is not often encountered in vacuum practice; however, two noteworthy exceptions are in ejector pump design and in the flow of gas from the atmosphere through a small hole into a vacuum. Turbulent flow will not be considered quantitatively here.

The most important cases in vacuum practice are those of molecular flow and effusion.

(*a*) **Aperture in a thin wall connecting two vessels which are large compared with the maximum aperture dimension** (Fig. 1.6(*a*)). In the molecular effusion case, the net throughput Q is given by

$$Q = \sqrt{\frac{\mathbf{k}T}{2\pi m}}\,(p_1 - p_2)A = \sqrt{\frac{\mathbf{R}T}{2\pi M}}(p_1 - p_2)A \qquad (1.9)$$

where $\mathbf{k}$ is Boltzmann's constant ($= 1{\cdot}38 \times 10^{-16}$ erg deg^{-1}), $\mathbf{R}$ is the gas constant ($= 8{\cdot}314 \times 10^7$ erg deg^{-1} mol^{-1}) (*see* Appendix A), T is the temperature in degrees Kelvin, m is the mass of the gas molecule, M is the molecular weight, A the area of the aperture in sq cm, p_1 is the higher pressure on one side of the aperture and p_2 the pressure on the other side. If p_1 and p_2 are in dyne/cm^2 *i.e.* microbars, then Q is given in c.g.s. units. If p_1 and p_2 are in torr, then Q is given in millilitre torr per sec.

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* *See* § 1.9 for comments on this equation.

Substitute $R = 8{\cdot}314 \times 10^7$, and take the temperature as 20° C, *i.e.* 293° K, then

$$Q = \sqrt{\frac{8{\cdot}314 \times 10^7 \times 293}{2\pi}}\,\frac{p_1 - p_2}{\sqrt{M}}\,A \text{ ml torr/sec}$$

if p_1 and p_2 are in torr.

$$\therefore \quad Q = \frac{62{\cdot}5}{\sqrt{M}}(p_1 - p_2)A \text{ litre torr/sec} \qquad (1.10)$$

at 20° C.

For air, considered as a nitrogen–oxygen mixture, put $M = 29$ (*see* Appendix A).

$$\therefore \quad Q = \frac{62{\cdot}5}{\sqrt{29}}(p_1 - p_2)A = 11{\cdot}6(p_1 - p_2)A \text{ litre torr/sec} \qquad (1.11)$$

Applying equation (1.4), the conductance U of such an aperture becomes, at 20° C.

$$U = \frac{62{\cdot}5A}{\sqrt{M}} \text{ litre/sec} \qquad (1.12)$$

or, for air,

$$U = 11{\cdot}6A \text{ litre/sec} \qquad (1.13)$$

Expressions such as (1.12) and (1.13) for conductances are convenient because the conductance is independent of the pressure—*provided that molecular pressures are concerned*—and depends only on the nature of the gas, the temperature and the dimensions of the aperture.

Note that result (1.13) implies that, at molecular pressures, air at 20° C *cannot flow through an aperture in a thin wall at a rate greater than 11·6 litre/sec/cm*^{2}. This is of fundamental importance in deciding the overall physical dimensions of the inlet port to a diffusion pump (§ 2.9). This result is also significant in discussing the feed-through of a sheet-like material into a vacuum system in industrial apparatus for continuous vacuum processing. For example, the possibility exists of passing capacitor paper from a roll through a slot in rubber into a vessel where vacuum deposition of a metal takes place (§ 10.6). This will best be carried out by arranging to pass the paper first into a rough vacuum region—maintained by a rotary pump—and then into the high vacuum—maintained by a diffusion pump—where the coating is done. The order of magnitude of the pumping speed required at the high-vacuum vessel would be primarily decided by the rate of leak of air from the rough vacuum into the high vacuum in accordance with the equation (1.13). Thus, if the slit in the rubber seal were l cm long and d cm wide, where d is very small, molecular flow would prevail because, even at rough vacuum pressures of the order of 1 torr, the mean free path λ would be greater than d. The leak rate would then be given by $11{\cdot}6\,ld$ litres per sec, the pressure concerned being the rough vacuum pressure.

(*b*) **Long tube of circular cross-section connecting two large vessels** (Fig. 1.6(*b*)). The net throughput Q in the molecular flow case is given by:

$$Q = \frac{1}{6}\sqrt{\frac{2\pi \mathbf{R}T}{M}}\,\frac{D^3}{L}(p_1 - p_2) \qquad (1.14)$$

where D is the diameter and L is the length of the tube in cm; the other symbols have the same meaning as in equation (1.9). Q is given in millilitre torr per sec if p_1 and p_2 are in torr. It is here assumed that L is considerably greater than D so that the impedance to gas flow of the entrance to the tube from the vessel at the higher pressure is negligible compared with the impedance of the tube itself.

Substituting $\mathbf{R} = 8{\cdot}314 \times 10^7$ and $T = 293°\ K$ (*i.e.* 20° C)

$$\therefore \quad Q = \frac{1}{6}\sqrt{\frac{2\pi \times 8{\cdot}314 \times 10^7 \times 293}{M}}\,\frac{D^3}{L}(p_1 - p_2)$$

$$= 65\frac{D^3}{\sqrt{ML}}(p_1 - p_2) \text{ litre torr/sec} \qquad (1.15)$$

For air, put $M = 29$, therefore,

$$Q = \frac{12{\cdot}1 D^3}{L}(p_1 - p_2) \text{ litre torr/sec} \qquad (1.16)$$

The conductance U at 20° C is then given by equation (1.4) as:

$$U = \frac{65 D^3}{L\sqrt{M}} \text{litre/sec} \qquad (1.17)$$

or, for air, as

$$U = \frac{12{\cdot}1 D^3}{L} \text{ litre/sec} \qquad (1.18)$$

Alternatively, putting $D = 2R$, where R is the radius of the tube,

$$U = \frac{8 \times 12{\cdot}1 R^3}{L} \simeq \frac{100 R^3}{L} \text{ litre/sec} \qquad (1.19)$$

an easily remembered and useful formula.

In the case of **viscous flow** through a long tube, Poiseuille's equation applies, and

$$U = \frac{\pi D^4}{128\eta L}\bar{p} \text{ c.g.s. units} \qquad (1.20)$$

where η is the viscosity of the gas in poise (*see* Appendix A), $\bar{p}$ is the average pressure in microbars, and D and L are the diameter and length, respectively, of the tube in cm.

For air at 20° C, this becomes

$$U = \frac{182\ D^4}{L}\bar{p} \text{ litre/sec} \qquad (1.21)$$

where $\bar{p}$ is now in torr.

Semi-empirically derived equations for the intermediate case between viscous and molecular flow have been given in the literature (Knudsen, K1; Loeb, L1), but are not frequently employed in vacuum practice in the laboratory, although they are useful to the pump designer and in large-scale vacuum systems. These equations are not quoted here, but some practical data is given in Table 1.5 and in Fig. 1.4 (*see also* Santeler, S1; Günther, Jaeckel and Oetjen, GJO1).

(*c*) **Short tube of circular cross-section connecting two large vessels** (Fig. 1.6(*c*)). By a short tube is meant one of which the length L is not large compared with the diameter D, or, alternatively, is smaller than D. In this case the impedance of the entrance aperture to the tube is significant compared with the tube itself.

To deduce the appropriate formula consider, in accordance with equation (1.7) for conductances in series, that

$$\frac{1}{U} = \frac{1}{U_{\text{ap}}} + \frac{1}{U_{\text{tube}}}$$

where U is the total conductance, whilst U_{ap} and U_{tube} are the conductances of the aperture and tube respectively.

$$\therefore \quad \frac{1}{U} = \frac{1}{\sqrt{\dfrac{\mathbf{R}T}{2\pi M}}A} + \frac{1}{\dfrac{1}{6}\sqrt{\dfrac{2\pi\mathbf{R}T}{M}}\dfrac{D^3}{L}} \qquad (1.22)$$

on applying equations (1.9) and (1.14).

Putting $A = \dfrac{\pi D^2}{4}$, as the tube entrance is circular, it follows that the ratio r of the conductance of the entrance aperture to that of the length of the tube is given by

$$r = \frac{U_{\text{ap}}}{U_{\text{tube}}} = \frac{\sqrt{\dfrac{\mathbf{R}T}{2\pi M}}\cdot\dfrac{\pi D^2}{4}}{\dfrac{1}{6}\sqrt{\dfrac{2\pi\mathbf{R}T}{M}}\cdot\dfrac{D^3}{L}} = \frac{3L}{4D} \qquad (1.23)$$

The equation for the conductance of the short tube can therefore be written as:

$$U = \frac{U_{\text{tube}} \times U_{\text{ap}}}{U_{\text{tube}} + U_{\text{ap}}} = \frac{\left(\dfrac{1}{6}\sqrt{\dfrac{2\pi\mathbf{R}T}{M}}\dfrac{D^3}{L}\right)^2 \times \dfrac{3L}{4D}}{\dfrac{1}{6}\sqrt{\dfrac{2\pi\mathbf{R}T}{M}}\dfrac{D^3}{L}\left(1 + \dfrac{3L}{4D}\right)}$$

$$= \frac{1}{6}\sqrt{\frac{2\pi\mathbf{R}T}{M}}\,\frac{D^3}{L}\left(\frac{1}{\dfrac{4D}{3L} + 1}\right) \qquad (1.24)$$

At a temperature of 20° C, *i.e.* $T = 293°$ K, substituting $\mathbf{R} = 8{\cdot}314 \times 10^7$, this becomes

$$U = \frac{65 D^3}{L\sqrt{M}}\left(\frac{1}{\dfrac{4D}{3L} + 1}\right) \text{ litre/sec}$$

$$= \frac{65 D^3}{\sqrt{M}}\left(\frac{1}{L + \dfrac{4D}{3}}\right) \qquad (1.25)$$

(*cf.* equation 1.15).

For air at 20° C, put $M = 29$,

$$\therefore \quad U = 12{\cdot}1D^3\left(\frac{1}{L + \dfrac{4D}{3}}\right) \text{ litre/sec} \qquad (1.26)$$

In high-vacuum practice, this is the most frequently encountered equation for conductances.

If the inside diameter D and the length L of the tube are measured in feet, then, for air:

$$U = 13{\cdot}3\left(\frac{D^3}{L + 0{\cdot}1D}\right) \text{ cu ft/min} \qquad (1.27)$$

Equation (1.22) can be expressed in an alternative form as:

$$U = \frac{\left(A\sqrt{\dfrac{\mathbf{R}T}{2\pi M}}\right)^2 \times \dfrac{4D}{3L}}{A\sqrt{\dfrac{\mathbf{R}T}{2\pi M}}\left(1 + \dfrac{4D}{3L}\right)}$$

where $A = \frac{\pi D^2}{4}$, the area of cross-section of the tube

$$\therefore \quad U = A\sqrt{\frac{\mathbf{R}T}{2\pi M}}\left(\frac{1}{1 + 3L/4D}\right)$$

which, on substituting $\mathbf{R} = 8{\cdot}314 \times 10^7$, becomes

$$U = 3{\cdot}638A\sqrt{\frac{T}{M}}\left(\frac{1}{1 + 3L/4D}\right) \text{ litre/sec} \qquad (1.28)$$

Clausing (C1) showed that equations (1.26), (1.27) and (1.28) are not exact because the aperture at the end of the circular tube cannot be treated simply as a series conductance.

It is preferable, therefore, to consider the problem from first principles. Suppose a tube connects a large reservoir X at a pressure p to another vessel Y at pressure p_1, where p_1 is at least an order of magnitude less than p. The flow of gas from X to Y will take place quite independently of the flow from Y to X because intermolecular collisions do not occur. A simplification which introduces no loss of generality is therefore to consider p_1 as zero. If there are n molecules per unit volume in the reservoir X and $\bar{v}$ is their average velocity, it is readily shown from the kinetic theory of gases (Appendix A) that the number of molecules N which enter the tube of cross-section area A per second is given by:

$$N = \tfrac{1}{4}n\bar{v}A \qquad (1.29)$$

Of these molecules, a fraction K will pass right through the tube, *i.e.* they will not collide with the walls. K is known as the **Clausing factor** and can be shown to be a function of L/r only for a cylindrical tube of length L and radius r. K can be defined as the average probability that a molecule which passes the entrance aperture to the tube will succeed in reaching Y without being returned to the reservoir. The number of molecules which leave the tube exit aperture per second is therefore $n\bar{v}AK/4$.

From equation (1.4) it is known that the conductance U of the tube is related to the throughput Q by

$$U = Q/p$$

The throughput is pV (Equation 1.1), where V is the volume of gas withdrawn per second from the reservoir. This volume is $\bar{v}AK/4$. Hence,

$$U = \bar{v}AK/4$$

In the kinetic theory of gases (Appendix A) it is established that

$$\bar{v} = \sqrt{\frac{8\mathbf{R}T}{\pi M}}$$

where $\mathbf{R}$ is the gas constant, T is the absolute temperature and M is the molecular weight of the gas. Hence

$$U = \sqrt{\frac{4{\cdot}16 \times 10^7}{\pi}}\sqrt{\frac{T}{M}}AK \text{ cu cm/sec}$$

on substituting $R = 8{\cdot}31 \times 10^7$.

$$\therefore \quad U = 3{\cdot}64\sqrt{\frac{T}{M}}AK \text{ litre/sec} \qquad (1.30)$$

For air at 20° C, *i.e.* 293° K, putting $M = 29$,

$$C = 11{\cdot}6\ AK \text{ litre/sec} \qquad (1.31)$$

The Clausing factor K is given approximately by $\dfrac{1}{\left(1 + \dfrac{3L}{4D}\right)}$ from equation (1.28) but more exactly by Table 1·4 (Dushman, D1).

The error involved in using equation (1.28) instead of the correct equation (1.31) may be obtained from the graph of Fig. 1.2.

Oatley (O1) made a series of experimental determinations of the conductances of tubes of circular cross-section. He gives the following theoretical and experimental values of K, designated by K_T and K_E respectively.

L/D	K_T	K_E	
		(*a*)	(*b*)
1	0·514	0·487	0·516
2	0·358	0·359	0·341
3	0·281	0·251	0·251
4	0·231	0·228	0·214
5	0·197	0·178	0·173

The results given in column (*a*) were obtained using pressures about 10 times as great as those used to obtain the values shown under (*b*).

After tracing small sources of error in his apparatus, Oatley considers that the agreement between the experimental and theoretical values is satisfactory.

TABLE 1.4

Values of the Clausing factor *K* for cylindrical tubes with various values of *L*/*D*

L/D	K
0	1
0·1	0·909
0·2	0·834
0·3	0·771
0·4	0·718
0·5	0·672
0·6	0·632
0·7	0·597
0·8	0·566
0·9	0·538
1·0	0·514
1·1	0·491
1·2	0·471
1·3	0·453
1·4	0·436
1·5	0·421
1·6	0·406
1·7	0·393
1·8	0·381
1·9	0·370
2·0	0·359
2·5	0·315
3	0·281
4	0·232
5	0·197
6	0·172
7	0·152
8	0·137
9	0·124
10	0·114
15	0·0797
20	0·0613
30	0·042
40	0·0319
50	0·0258
100 and above use equation (1.17)	

A chart from which the conductance *U* of a cylindrical tube in litre/sec for air at 20° C can be read is given in Fig. 1.3. This chart is deduced from equation (1.26).

Table 1.5 gives the conductances (admittances) for air for various diameters between 0·5 in. and 25 in. for tube lengths between 1 in. and 16 ft and pressures between 10^{-4} and 10 torr. The left half of the table gives the conductances of conduits in torr cu ft/min per torr pressure difference (*i.e.* cu ft/min) at 10^{-4} torr. Thus, the conductance of a 6 in. diameter conduit of length 4 ft is found to be 500 in the left-hand half of the table (it is marked **) and if the conductance of the same conduit is required at 0·1 torr, then the factor given is 32. This is found on the right-hand half of the table and gives a value of 16,000 cu ft/min. The figures in brackets marked with a single asterisk refer to lengths in inches instead of feet. Thus the conductance of a tube 1 in. long and 0·5 in. diameter is 15 cu ft/min, from the figure in brackets at the top of the second column.

This Table (1.5) is very convenient because it gives the values of the conductances of tubes in the intermediate and viscous flow pressure regions as well as in the molecular flow region. Note the much greater conductances of tubes at the higher pressures. Compare the formula (1.20) which indicates that, in the viscous flow region, the conductance increases with mean pressure.

For convenient and rapid evaluation of conductances, an *abac* (*see* Pirani and Fischer, PF1, based on Brown, Di Nardo, Cheng and Sherwood, BDCS1)

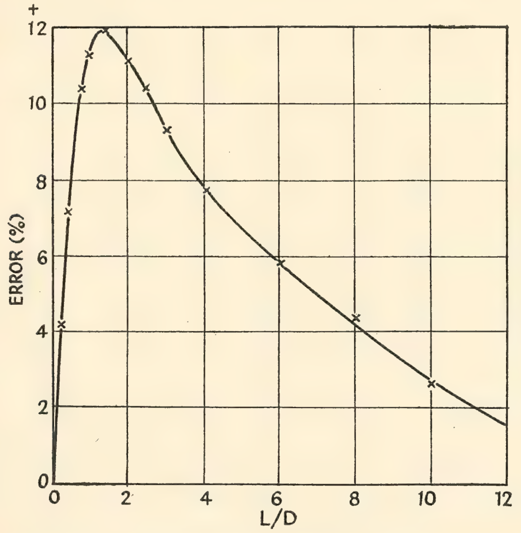


FIG. 1.2 Plot of *L*/*D* against the percentage error involved in using equation (1.28)

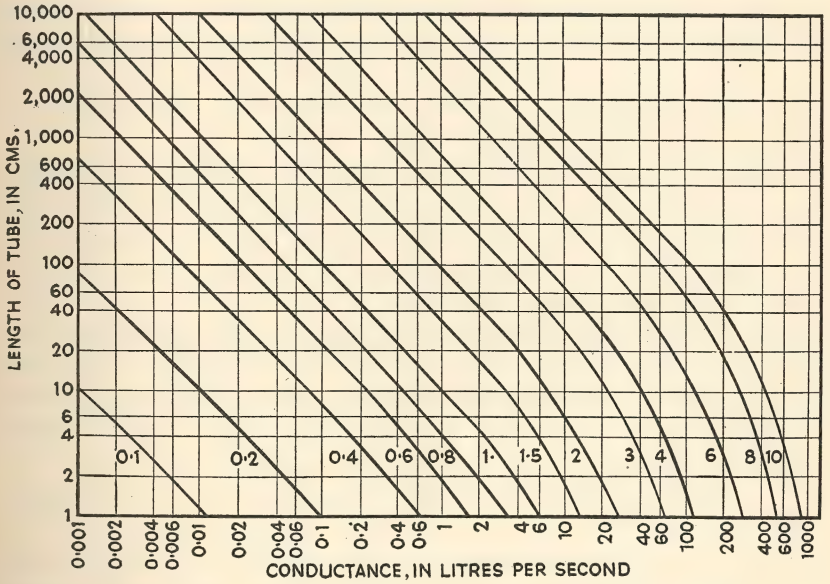


FIG. 1.3 The conductance *U* in litre/sec for air in the case of cylindrical tubes (parameter is diameter of tube in cm)

TABLE 1.5

Conductances for air of cylindrical tubes of various lengths and diameters and at various pressures

Dia in.	Conductances at 10^{-4} torr					Multiplying factor at given pressure				
	Length in feet					torr				
	1	2	4	8	16	10^{-3}	10^{-2}	10^{-1}	1	10
0·5	2·2 (15*)	1·2 (9·5*)	0·6 (5·5*)	0·3	0·15	1	1·2	3·7	32	320
1	10 (63*)	5·5 (36*)	2 (25*)	1·5	0·75	1	1·4	6	55	550
2	70	40	22	11	5·5	1	2	12	110	1,100
4	400	250	140	80	40	1·01	3	21	210	2,100
6	1,200	800	500**	250	130	1·1	3·8	32**	320	3,200
12	7,000	4,500	3,000	1,800	1,000	1·4	7	62	620	6,200
16	15,000	10,000	6,500	4,000	2,200	1·6	9	85	850	8,500
24	35,000	26,000	19,000	12,000	7,000	1·9	13	130	1,300	13,000

is given in Fig. 1.4. Consider the determination of the conductance of a cylindrical tube of length 4 ft and diameter 6 in., using this *abac*. A ruler is placed across the three scales of Fig. 1.4(*a*) so that it intersects the scale marked L (ft) at 4 and the scale marked D (inch) at 6. The scale U_M—conductance to molecular flow—is then intersected at 500, showing that the conductance of the tube is 500 cu ft/min. If, now, the conductance U of this same tube is required at, say, 10^{-1} torr, then the multiplying factor required is determined from the *abac* of Fig. 1.4(*b*); a ruler is placed across the scales so that it intersects the scale marked p at 10^{-1} torr and the scale D at 6 in., giving a factor U/U_M of 32, so that the conductance in cu ft/min at a pressure of 10^{-1} torr is therefore 16,000 cu ft/min.

It might be thought that Table 1.5 and the charts of Fig. 1.4 were denying the assertion of § 1.5(*a*) that the conductance is independent of the pressure. This statement is, however, only true for molecular flow. The table and *abac*s given extend well into the intermediate and viscous flow regions where the conductance becomes pressure dependent.

(*d*) **Formulae for the conductances to molecular flow of pipes and ducts other than those of simple circular cross-section area.** Knudsen (*see* Guthrie and Wakerling, GW1) gives a general formula for the case of a pipe of uniform cross-section area A, perimeter of the cross-section B, and length of the pipe L. The conductance

$$U = \frac{16}{3}\alpha\sqrt{\frac{\mathbf{R}T}{2\pi M}}\,\frac{A^2}{BL}\text{ cu cm/sec} \qquad (1.32)$$

where α is a constant of proportionality depending on the relative dimensions of the cross-section area, **R** is the gas constant in erg deg^{-1} mol^{-1}, M is the molecular weight of the gas, and cm-units are used for A, B and L.

Substituting $\mathbf{R} = 8{\cdot}314 \times 10^7$ and $T = 20°\text{ C} \equiv 293°\text{ K}$,

then
$$U = \frac{16\alpha}{3}\sqrt{\frac{8{\cdot}314 \times 10^7 \times 293}{2\pi M}}\,\frac{A^2}{BL}\text{ cu cm/sec}$$

$$= \frac{1000\alpha}{3\sqrt{M}}\,\frac{A^2}{BL}\text{ litre/sec} \qquad (1.33)$$

For air at 20° C, putting $M = 29$, this becomes

$$U = 62\alpha\,\frac{A^2}{BL}\text{ litre/sec}$$

For a pipe formed by the annulus between coaxial cylindrical tubes (Fig. 1.6(*d*)), let D_1 = outer tube internal diameter, D_2 = inner tube external diameter and L the length of the tubes. Then A, the cross-section area of the annulus, is $\frac{\pi}{4}(D_1^2 - D_2^2)$ whilst B, the perimeter of the cross-section, is $\pi(D_1 + D_2)$. Substituting these values for A and B in equation (1.33) gives:

$$U = \frac{1000\alpha}{3\sqrt{M}}\,\frac{\pi^2(D_1^2 - D_2^2)^2}{16\pi(D_1 + D_2)L}\text{ litre/sec}$$

$$= \frac{1000\alpha\,(D_1 - D_2)^2\,(D_1 + D_2)}{48L\pi\sqrt{M}}\text{ litre/sec at 20° C} \qquad (1.34)$$

D and L being in cm.

It is here assumed that L is considerably greater than D, so that the inlet aperture plays an insignificant part in impeding the gas flow compared with the length of the duct. Barrett and Bosanquet (BB1) give α as a function of D_2/D_1 in the form of Table 1.6 (*see also* Guthrie and Wakerling, GW1).

TABLE 1.6

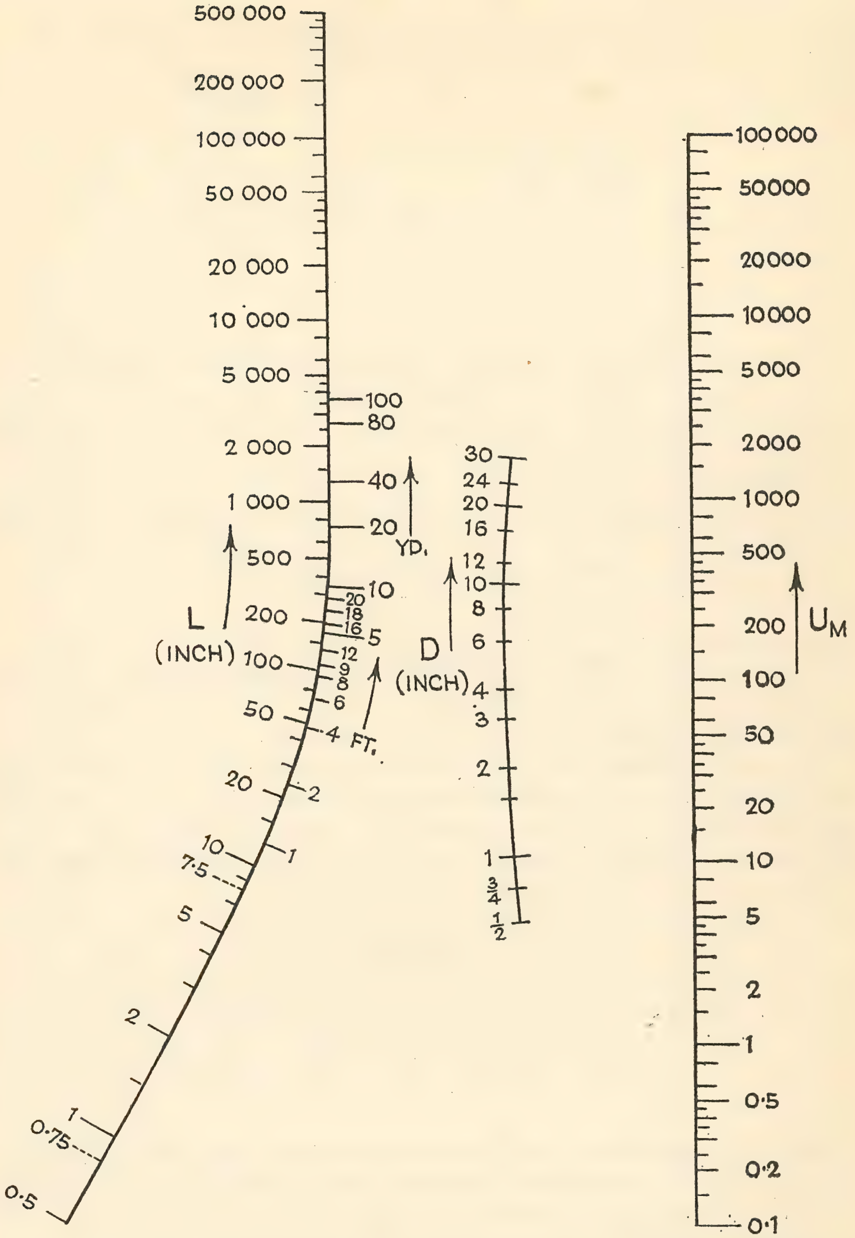
D_2/D_1	0	0·26	0·5	0·7	0·87	0·97
α	1	1·07	1·15	1·25	1·43	1·68

For a rectangular duct, suppose the lengths of the sides of the rectangular cross-section are a and b in cm. Then in equation (1.32) the cross-section area $A = ab$, whereas the perimeter $B = 2(a + b)$. Hence, equation (1.33) becomes

$$U = \frac{1000\alpha}{3\sqrt{M}}\,\frac{a^2b^2}{2(a + b)L}$$

$$= \frac{1000\alpha}{6\sqrt{M}}\,\frac{a^2b^2}{(a + b)L}\text{ litre/sec at 20° C} \qquad (1.35)$$

where L is the length of the duct.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10
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2
1
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0·2
0·1
U_M

FIG. 1.4(*a*) *Abac* giving the molecular conductances, U_M, of straight cylindrical tubes at a pressure of 10^{-4} torr or below

Values of α concerned in this case are given in Table 1.7 (Barrett and Bosanquet, BB1).

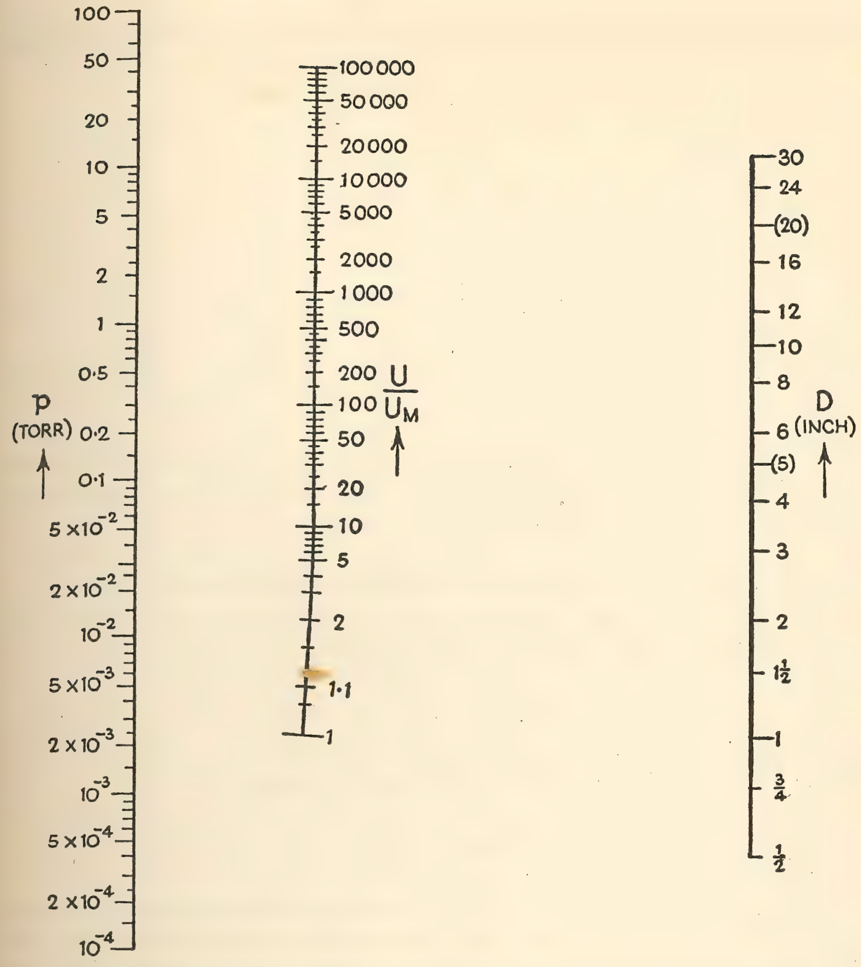
100
50
20
10
5
2
1
0·5
P
(TORR)
0·2
0·1
5×10^{-2}
2×10^{-2}
10^{-2}
5×10^{-3}
2×10^{-3}
10^{-3}
5×10^{-4}
2×10^{-4}
10^{-4}
100 000
50 000
20 000
10 000
5 000
2000
1 000
500
200
100
50
20
10
5
2
1·1
1
$\frac{U}{U_M}$
30
24
(20)
16
12
10
8
6
(5)
4
3
2
$1\frac{1}{2}$
1
$\frac{3}{4}$
$\frac{1}{2}$
D
(INCH)

FIG. 1.4(*b*) Multiplication factors, U/U_M, for pressures above 10^{-4} torr; U_M obtained from Fig. 1.4(*a*)

Oatley (O1, O2) measured *K*, the Clausing factor, for various ducts not having a simple circular cross-section. For rectangular tubes, *K* was found to have nearly the same values as for circular tubes of the same cross-sectional area. It is therefore suggested that equations (1.30) and (1.31) be used in conjunction with Table 1.4 for ducts of rectangular cross-section. For the annular space between concentric cylinders, equations (1.30) and (1.31) also apply but where *K* is given by Table 1.8.

TABLE 1.7

b/a	1	0·667	0·5	0·333	0·2	0·125	0·1
α	1·11	1·13	1·15	1·2	1·3	1·4	1·44

Oatley also found *K* for a right-angle bend of circular cross-section to be 0·30 by experiment. The mean length of the path through the axis of the bent

TABLE 1.8 (Oatley O1)

Values of *K* for the annular space between concentric cylinders (experimentally determined)

Length ÷ External radius	External ÷ internal radius				
	3·02	2·4	2·0	1·71	1·5
	K	*K*	*K*	*K*	*K*
1	0·59	0·56	0·54	0·51	0·47
2	0·42	0·39	0·37	0·34	0·31
4	0·26	0·24	0·23	0·20	0·18
6	0·19	0·18	0·16	0·15	0·13
8	0·15	0·14	0·13	0·11	0·10
10	0·12	0·11	0·10	0·09	0·08

tube was four times the radius. Clausing's value of K for a cylindrical tube with length/radius of 4 is 0·359. It is concluded that the effect of bending the tube through a right-angle is small.

1.6. The Effect of the Impedance of Tubulation on the Speed of a Pump

If S is the actual speed of a pump at its inlet port and U is the conductance of the tubing between the pump and the vacuum tank, then

$$\frac{1}{S_E} = \frac{1}{S} + \frac{1}{U} \qquad (1.36)^*$$

where S_E is the effective speed of the pump at the tank.

Thus
$$S_E = \frac{SU}{S+U} \qquad (1.37)$$

The maximum attainable value of S_E is equal to U, the tube conductance. Thus, consider that a very fast pump is used so that S is a large number. Then U is negligible compared with S in the denominator of equation (1.37) and the expression becomes $SU/S = U$. This is a very important practical point, *viz.* that the *effective pumping speed cannot exceed the rate at which gas can flow through the tube connecting the pump and the vessel.* For example, in pumping a radio valve, it is necessary to have a narrow exhaust stem with a constriction in it for subsequent seal-off from the pumps. Such a tube has a very small conductance. If a value for S is chosen which is, say, 5 times U, the conductance of this tube—a figure readily obtainable with a small pump—then, substituting in equation (1.37) gives $S_E = 5U^2/6U = \frac{5}{6}U$. *To choose a much larger pump is a waste of money.* Thus, if S were equal to $100U$, S_E would still only be $\frac{100U^2}{101U}$, *i.e.* only 16% faster than in the previous case.

A further illustration of the importance of equation (1.37) is to consider a large kinetic vacuum system employing a pump of a speed, say, 1000 litre/sec.

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* *See* § 1.9 for comments on this equation.

If it is required to ensure that the impedance of the tube connecting the pump to the vessel does not reduce this speed by more than, say, 40%, then

$$S_E = 0{\cdot}6S$$

Hence, using equation (1.37)

$$S_E = \frac{SU}{S+U} = 0{\cdot}6S$$

$$\therefore \quad U = 1{\cdot}5S$$

i.e. the conductance of the tube must be 1500 litre/sec.

Suppose the pressure is 10^{-4} torr, *i.e.* molecular flow conditions prevail, and the pump is an oil-diffusion pump with an inlet port diameter of 9 in. and the required speed of 1000 litre/sec. A 9-in. diameter connecting tube to the vacuum tank is chosen for convenience, with a conductance of 1000 litre/sec = 2120 cu ft/min (*see* Table 1.3). A ruler placed across the *abac* of Fig. 1.4(*a*) then shows that the connecting tube must not be longer than 2 ft. On the other hand, if the connecting tube is only 6 in. diameter, then the *abac* indicates that its length must not exceed 3 in.

It frequently happens, owing to the disposition of the diffusion pump with respect to the tank, that a right-angle or other bend is necessary in the tubing connecting these two. It is not worth while evaluating the correct formula in such cases. It is satisfactory to add to the total length of the pipe measured along its axis a length equal to the inside diameter of the pipe, if the bend is a right-angle or of small radius (*cf.* Oatley's results quoted in § 1.5). For gradual bends in pipes of large diameter it is satisfactory simply to use the axial length of the pipe in the conductance formulae.

Although it is now fairly widely appreciated by vacuum technicians that it is essential to use wide bore, short connecting tubes between the diffusion pump and the tank, especially when large kinetic systems are erected, it is felt that the influence of connecting tubing on the speed of a mechanical rotary pump, especially when used as a fore-pump to a diffusion pump, is often overlooked (*see* § 1.8).

1.7 Pump-down Time

The time required for a pump of given effective speed S_E to pump a tank of known volume V from a pressure p_1 down to a pressure p_2 can be calculated as follows.

Suppose S_E is the effective speed, *i.e.* the speed at the tank taking into account the restriction to gas flow due to the connecting tubing.

At a pressure p, the throughput $Q = pS_E$, hence

$$Q = pS_E = \frac{-d}{dt}(pV) = -V\frac{dp}{dt}$$

because the vessel volume V is a constant.

$$\therefore \quad \frac{dp}{p} = \frac{-S_E}{V}\,dt$$

Integrating

$$\log_e p = \frac{-S_E t}{V} + \text{const.}$$

When $t = 0$, $p = p_1$, the initial pressure before pumping begins.

$$\therefore \quad \log_e p = \frac{-S_E t}{V} + \log_e p_1$$

$$\therefore \quad t = \frac{V}{S_E} \log_e \frac{p_1}{p_2}$$

where t is the time required to attain the pressure p_2.

$$\text{i.e.} \quad t = 2{\cdot}3 \frac{V}{S_E} \log_{10} \frac{p_1}{p_2} \qquad (1.38)$$

If V is in litres, S_E in litre/sec, and p_1 and p_2 are in the same pressure units, then t, the time required, is given in seconds.

It has been assumed here that S_E is known whereas, in fact, it is dependent on the pressure. For approximate calculations where the conductance of the connecting tubing is large compared with S, the actual pump speed, S_E can be put equal to S and S determined from the pump characteristic as the mean of the speeds at p_1 and p_2. In any case, the time calculated will usually be too small since it is assumed that only air is being pumped away if the speed figures used are for air. In practice, the results obtained are very inaccurate at diffusion pump pressures ($< 10^{-4}$ torr), though they are reasonably accurate for the determination of the time of exhaust, using a mechanical rotary pump, provided that the final pressure p_2 required is not less than ten times the ultimate pressure provided by such a pump. If p_2 is too near this ultimate, then the effect of the vapour pressures of water vapour present and of the pump oil will mean that much longer pump-down times are demanded than are indicated by evaluation using equation (1.38).

1.8. Matching of Diffusion Pump and Backing Pump

In a vacuum system—especially a kinetic system—where a mechanical rotary pump is required to 'back' a diffusion pump, it is essential, for efficient operation, that the required fore-pressure be maintained throughout the pumping schedule. In this connection, the following definitions of terms are valuable*:

Limiting forepressure—the forepressure above which the intake or fine side pressure to the diffusion pump has increased by more than a few tenths of a micron.

Breaking forepressure—the forepressure above which the intake pressure to the diffusion pump has increased by more than a factor of ten.

Tolerable forepressure—the forepressure above which the intake pressure has increased by more than ten per cent.

These terms arise from the fact that the speed and intake pressure of a diffusion pump are both dependent on the forepressure provided. If this forepressure is exceeded, then decrease of speed and increase of intake pressure occur. The so-called tolerable forepressure must hence be maintained during the pumping schedule if the vacuum in the vessel is to be satisfactorily maintained.

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* Based on *British Standards Institution, 'Terms Used in High Vacuum Technology'* B.S.2951: 1958.

Suppose the throughput of the vacuum system is Q, which equals pV (§ 1.4). If p_D is the intake or fine-side pressure provided at the vessel by the diffusion pump, and the speed of the diffusion pump (including the impedance of the tubing) is S_D, then

$$Q = p_D S_D.$$

This throughput must be handled by the fore-pump. If it is not, then a pressure rise will occur in the line between the fore-pump and the diffusion pump. If this rise transcends the tolerable forepressure, the fine-side pressure will also rise and the speed there will fall.

Suppose the forepressure needed is p_F. Let the speed of the fore-pump be S_F at this pressure, then

$$Q = p_D S_D = p_F S_F$$

$$\text{or} \quad S_F = \frac{p_D S_D}{p_F} \qquad (1.39)$$

gives the required speed S_F of the fore-pump. This speed must, of course, take into account the impedance of the connecting tube, valves, etc., between the fore-pump and the diffusion pump.

As an example, consider that a speed of 5000 litre/sec must be maintained at the vessel at a pressure of 10^{-4} torr. The throughput Q is then

$$Q = 5000 \times 10^{-4} = 5 \times 10^{-1} \text{ litre torr/sec.}$$

Suppose the tolerable forepressure p_F is 10^{-1} torr. Then, the effective fore-pump speed S_F must be given by

$$S_F p_F = 5 \times 10^{-1}$$

$$\therefore \quad S_F = \frac{5 \times 10^{-1}}{10^{-1}} = 5 \text{ litre/sec} = 300 \text{ litre/min}$$

$$= 300 \times 0{\cdot}0353 = 10{\cdot}59 \text{ cu ft/min}$$

(*see* Table 1.3).

A Kinney pump VSD778 is available which has a speed of 16 cu ft/min at a pressure of 10^{-1} torr. The smaller Kinney pump, VSD556, with a speed of 8 cu ft/min at this pressure, would be too small.

Consider now, however, the conductance of the tubing between the Kinney pump and the diffusion pump. Let this be U. Then using equation (1.37).

$$S_E = \frac{S_F U}{S_F + U}$$

where S_E is the effective speed of the fore-pump at the diffusion-pump outlet. If it is required to maintain S_E at 11 cu ft/min, whereas the pump unrestricted gives 16 cu ft/min, then

$$11 = \frac{16U}{16 + U}$$

$$\therefore \quad U = 35 \text{ cu ft/min approx.}$$

Suppose that a tube of 2 in. bore connects the fore-pump and the diffusion pump. Its conductance at the pressure of 10^{-1} torr must be at least 35 cu ft/min. Reference to the *abac* (Fig. 1.4(*b*)) shows that, at a pressure of 10^{-1} torr and a tube diameter of 2 in., the multiplying factor U/U_M is 12. Referring to the *abac* (Fig. 1.4(*a*)), it follows that U_M on this chart must be 3 cu ft/min. Hence, a 2-in. diameter tube must not be more than 6 ft long. This is satisfactory for most applications. If, however, a ½-in. bore tube were chosen, then $\frac{U}{U_M}$ is 3·5 from Fig. 1.4(*b*), so U_M on Fig. 1.4(*a*) must be 10. It then follows that a ½-in. tube must not be more than 2 in. long; it is impossible to satisfy this requirement using large equipment because the outlet discharge pipe of the diffusion pump itself will be much longer than 2 in.

Provided due account of the impedance of the backing line tubing is made, the usual simple practice is to adopt the manufacturer's recommendations in regard to the choice of the fore-pump to match a particular diffusion pump.

It is becoming more customary for manufacturers to give curves of the throughput against pressure for vacuum pumps as well as speed against pressure. The throughput is usually given in gram/sec. This practice is a useful one, because it enables the matching of the correct fore-pump against the chosen diffusion pump to be decided quickly from the curves, provided that the effect of tubulation is subsequently calculated. Details are given in § 2.17.

A further development, apropos of ensuring that the throughput of gas handled by the diffusion pump is also handled by the fore-pump, has led to the introduction of ejector pumps (§ 2.18) and Roots pumps (§ 2.7). These are especially valuable in large kinetic systems where very considerable amounts of gas have to be handled.

1.9. Criticisms of Equations for Calculating the Molecular Flow of Gas through Composite Vacuum Systems

Oatley (O2) has recently put forward criticisms of the equation (1.7) for conductances in series and of equation (1.36) for evaluating the effective speed of a pump connected to the vacuum tank by a tube. He considers the case of two tubes of different lengths L_1 and L_2 but equal circular cross-sections of radius r and conductances U_1 and U_2, respectively, connected in series (Fig. 1.5). The usual practice is to apply equation (1.7):

$$\frac{1}{U}=\frac{1}{U_1}+\frac{1}{U_2} \tag{1.40}$$

where U is the overall conductance of the tubes when joined together. Now U_1 and U_2 are given by equation (1.30) where K_1 and K_2 are the corresponding Clausing factors. The Clausing factor K for the combined tubes of total length L should therefore be given by:

$$\frac{1}{K}=\frac{1}{K_1}+\frac{1}{K_2} \tag{1.41}$$

Oatley shows that this equation (1.41) does not hold. This is clear from the results given in Table 1.9, which is an abbreviated presentation from his paper.

TABLE 1.9
Comparison of calculated values of K

L_1/r	L_2/r	Clausing's values for			K calculated using equation 1.41	Error %
		K_1	K_2	K		
0·5	0·5	0·801	0·801	0·672	0·401	40·3
1	1	0·672	0·672	0·514	0·336	34·6
2	2	0·514	0·514	0·359	0·257	28·4
4	4	0·359	0·359	0·232	0·180	22·4
6	6	0·281	0·281	0·172	0·141	18·0
8	8	0·232	0·232	0·137	0·116	15·3
10	10	0·197	0·197	0·114	0·099	13·1
20	20	0·114	0·114	0·061	0·057	6·6
4	1	0·359	0·672	0·315	0·234	25·7
4	10	0·359	0·197	0·152	0·127	16·4

It is seen that errors of as much as 40% occur, whilst errors of the order of 20% are usual. As equation (1.41) is incorrect, it follows that equation (1.40) is invalid.

To arrive at a more accurate expression, Oatley considers the problem from first principles. Consider two circular cross-section tubes of the same radius joined together (Fig. 1.5). Let the Clausing factor for tube 1 be K_1 and for tube 2 be K_2. Suppose N molecules enter the left-hand end of 1 from a reservoir. Of the N molecules which enter 1, NK_1 pass into 2 and $N(1-K_1)$ are returned to the reservoir. Of the NK_1 which enter 2, NK_1K_2 emerge from the right-hand end of 2 whilst $NK_1(1-K_2)$ return to 1. Of these, $NK_1(1-K_2)(1-K_1)$ enter 2 again and $NK_1K_2(1-K_1)(1-K_2)$ emerge from the right-hand end of 2. It is readily seen that the total number of molecules passing right through the tube from left to right is given by

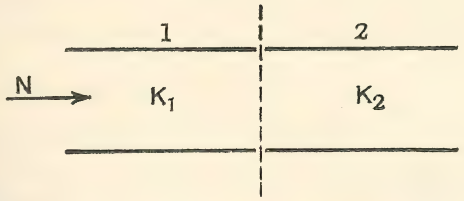


FIG. 1.5 Junction of two tubes of the same radius

$$NK = NK_1K_2[1+(1-K_1)(1-K_2)+(1-K_1)^2(1-K_2)^2+\ldots]$$

$$= \frac{NK_1K_2}{K_1+K_2-K_1K_2}$$

$$\therefore\quad \frac{1}{K}=\frac{1}{K_1}+\frac{1}{K_2}-1 \tag{1.42}$$

If this equation (1.42) is used to calculate the effect on the Clausing coefficient of combining two tubes in place of equation (1.41) in Table 1.6, the error involved is in no case greater than 6%.

In examining the physical explanation of the cause of the failure of equations (1.40) and (1.41), Oatley points out that the analogy usually made with a series electrical circuit is false because, at molecular pressures, the motion of each molecule is entirely independent of all other molecules. Therefore, true flow—as in gas at higher pressures or as in electric currents—does not exist. When the pressure is in the molecular region, the number of molecules crossing the junction between tubes 1 and 2 (Fig. 1.5) is quite different from the number flowing in the opposite direction. Hence, there is no unique value of the pressure at the junction, as must be assumed in deriving the equation (1.41).

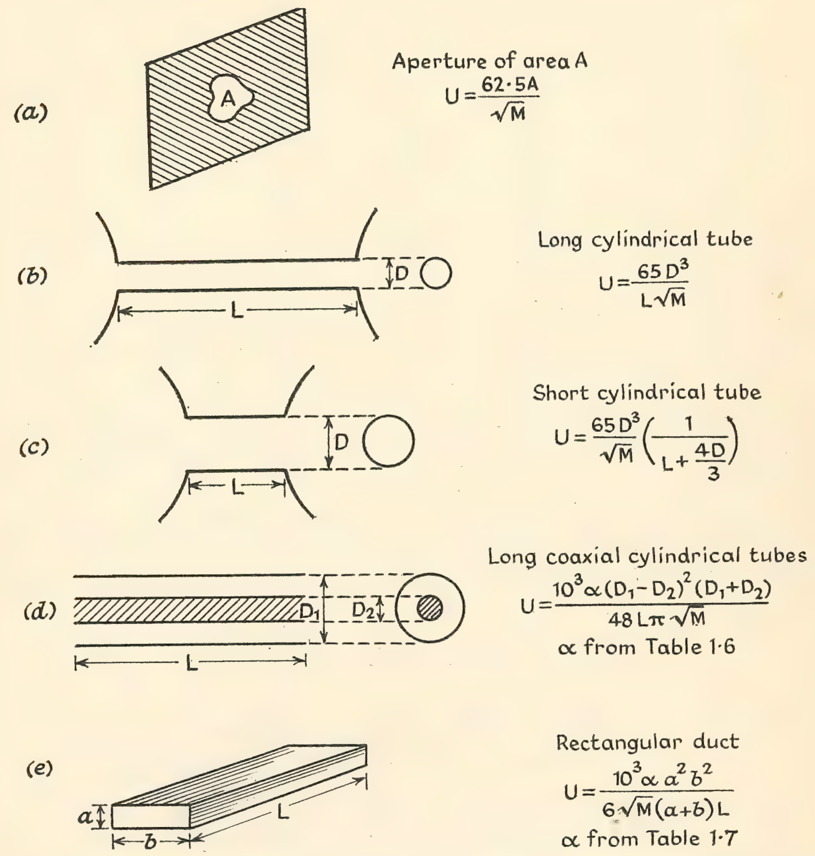

(a)
A
Aperture of area A
$U = \frac{62\cdot5A}{\sqrt{M}}$
(b)
D
L
Long cylindrical tube
$U = \frac{65D^3}{L\sqrt{M}}$
(c)
D
L
Short cylindrical tube
$U = \frac{65D^3}{\sqrt{M}}\left(\frac{1}{L+\frac{4D}{3}}\right)$
(d)
D_1
D_2
L
Long coaxial cylindrical tubes
$U = \frac{10^3\alpha(D_1-D_2)^2(D_1+D_2)}{48L\pi\sqrt{M}}$
α from Table 1·6
(e)
a
b
L
Rectangular duct
$U = \frac{10^3\alpha a^2b^2}{6\sqrt{M}(a+b)L}$
α from Table 1·7

FIG. 1.6 Molecular conductances of tubes and ducts. U is the molecular conductance in litre per sec at 20° C for gas of molecular weight M. Tube or duct dimensions in cm

Oatley further shows that similar objections can be made to calculations on the restriction of the speed of a pump due to the connecting tube to the vacuum tank (equation 1.36). Suppose the average probability that a molecule will enter the throat of a pump at molecular pressures is given by K_1. Let this pump be connected to a large vacuum tank by a tube for which the Clausing factor is K_2. For simplicity, let the area of cross-section of the tube and that of the pump throat both be A cm². If S is the speed of the pump, U the conductance of the connecting tube and S_E the effective speed at the vacuum tank, then for air at 20° C (*see* equation 1.31).

$$S = 11{\cdot}6AK_1$$

$$U = 11{\cdot}6AK_2$$

and

$$S_E = 11{\cdot}6AK$$

where K is the average probability that a molecule will enter the connecting tube and eventually pass through the pump.

The relation between K, K_1 and K_2 is given by equation (1.42) as

$$\frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2} - 1$$

$$\therefore \quad \frac{11{\cdot}6A}{S_E} = \frac{11{\cdot}6A}{S} + \frac{11{\cdot}6A}{U} - 1$$

i.e.

$$\frac{1}{S_E} = \frac{1}{S} + \frac{1}{U} - \frac{1}{11{\cdot}6A} \qquad (1.43)$$

is the corrected form of equation (1.31).

Oatley quotes a value of $K_1 = 0{\cdot}3$ from an examination of manufacturers' data on unbaffled oil diffusion pumps. The speed of a pump of throat area A cm² is hence approximately $11{\cdot}6 \times 0{\cdot}3A$, *i.e.* $3{\cdot}48A$ litre/sec. $\frac{1}{S}$ is therefore $\frac{1}{3{\cdot}48A}$ sec litre^{-1}. The correction term, $\frac{1}{11{\cdot}6A}$, can therefore amount to about 30% of $\frac{1}{S}$. In practice, errors of as much as 20% can arise in using equation (1.36) to calculate effective pump speeds.

Steckelmacher (S2) has criticized Oatley's analysis on the basis that the Clausing factor is concerned with the probability of molecules entering a tube from a *large vessel* and that any attempt to apply it to a tube having its mouth connected to the end of another tube involves inaccuracies. In the case of two tubes of equal cross-sectional area joined end-to-end (Fig. 1.5) Steckelmacher justifies the conventional approach to conductance calculations on the following lines. In place of equation (1.40), put

$$\frac{1}{U} = \frac{1}{U_A} + \frac{1}{U_{\text{tube 1}}} + \frac{1}{U_{\text{tube 2}}} \qquad (1.44)$$

where U_A is the conductance of the entrance aperture to tube 1, $U_{\text{tube 1}}$ is the conductance of tube 1 and $U_{\text{tube 2}}$ is the conductance of tube 2. Moreover,

$$\frac{1}{U_1} = \frac{1}{U_A} + \frac{1}{U_{\text{tube 1}}} \qquad (1.45)$$

and

$$\frac{1}{U_2} = \frac{1}{U_A} + \frac{1}{U_{\text{tube 2}}} \qquad (1.46)$$

Whereas equation (1.44) is correct, equation (1.40) is incorrect because, as is seen from equations (1.45) and (1.46), it includes $1/U_A$ twice. This entrance aperture impedance should *not* be included twice but only *once* because whereas the molecules enter tube 1 from a large vessel, *i.e.* they have to 'find' this first aperture, they enter tube 2 from the confines of tube 1, *i.e.* they do not have to 'find' the entrance to tube 2, indeed, they have a probability of unity of entering tube 2.

Hence, in writing the equation (1.41) for the Clausing factor of the combined tubes, *i.e.*

$$\frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2}$$

the effect of U_A has been included twice. Indeed, equation (1.41) will represent:

$$\frac{1}{U} = \frac{2}{U_A} + \frac{1}{U_{\text{tube 1}}} + \frac{1}{U_{\text{tube 2}}}$$

whereas equation (1.44) should be concerned. Equation (1.41) must therefore be written to take into account the fact that molecules leaving tube 1 will all enter tube 2, and it must be modified to give

$$\frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2} - 1$$

which is the same as equation (1.42) due to Oatley.

Steckelmacher's assertion is, therefore, that the conventional methods of calculating combinations of conductances are correct provided that a correct analysis of the impedances to gas flow of the constituent parts of the tubulation is made. The conventional methods will be used in this text.

2

VACUUM PUMPS

2.1. Mechanical Rotary Pumps

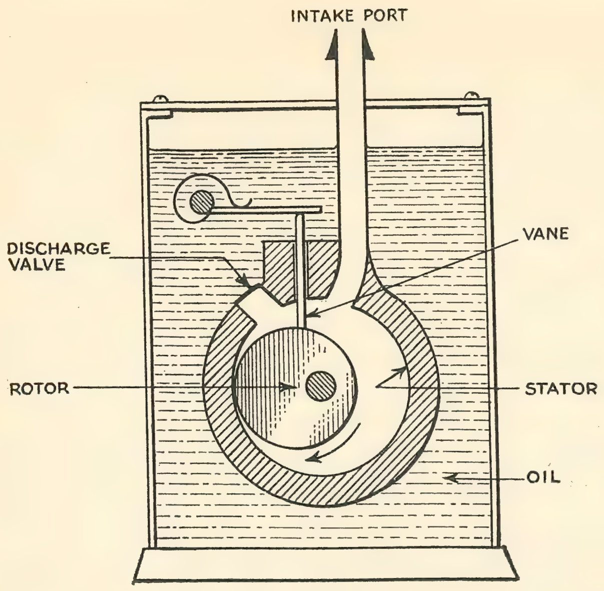
Details of the construction of the various patterns of rotary pumps are given in several texts (Dushman, D1; Jaeckel, J1; Yarwood, Y1). Fig. 2.1 illustrates the chief types.

For full details of construction and performance it is best to refer to the catalogues of the various manufacturers (*see* Appendix D). Several of these firms now supply small rotary pumps designed to be as *noiseless* as possible.

Single-stage and two-stage series-connected models are available. A single-stage model is capable—in most cases—of an ultimate pressure—*i.e.* the limiting pressure in the vacuum system after sufficient pumping time to establish that further reductions in pressure will be negligible—of 5×10^{-3} torr, whilst a two-stage pattern will reach 10^{-4} torr. Such pressures are attained working relative to the atmosphere, *i.e.* the discharge outlet is direct to the atmosphere, and are permanent gas pressures as registered for dry air using a McLeod gauge (§ 3.4). If the total pressure is recorded using, say, a Pirani gauge (§ 3.6) the ultimate recorded will be about 10^{-2} torr for a single-stage pump and 2×10^{-3} torr using a two-stage pump. These higher readings will be due to the vapour pressure of the sealing oil or its decomposition products in the pump. The ultimate air pressure recorded by a McLeod will only be reached if a small, leak-free vessel is being pumped and water vapour is removed as far as possible by a cold trap (§ 2.11) or a phosphorus pentoxide trap (§ 2.4).

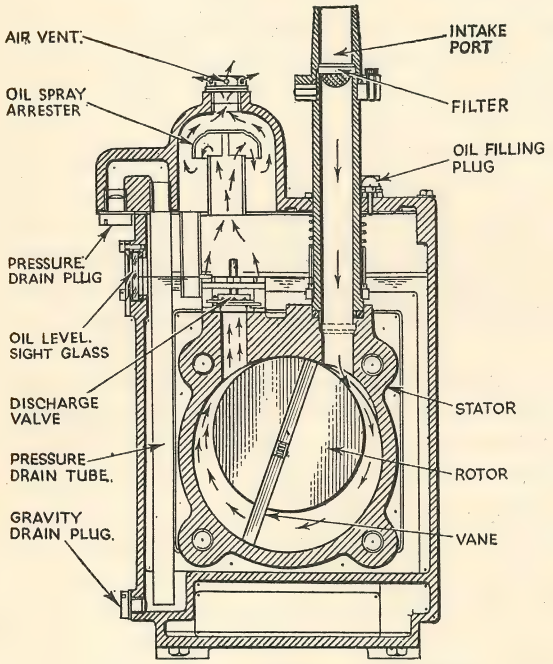
In a recent investigation of the ultimate pressure provided by a two-stage rotary pump, Hockly and Bull (HB1) show that decomposition of the oil into gases and lighter fractions brought about by localized high-temperature 'spots' in the pump is an important factor determining the ultimate. Where the vanes slide on the rotor, boundary lubrication prevails, *i.e.* the lubricating film is so thin as to be of molecular dimensions; the surfaces therefore slide upon one another at 'break-through' regions where surface asperities exist, resulting in high temperatures. The ultimate pressure recorded for a two-stage rotary pump was about 5×10^{-3} torr, using an Alphatron gauge (§ 3.11) calibrated for air. These authors suggest the possibility of finding suitable additives to the oil which will reduce or prevent this decomposition.

A wide range of mechanical rotary pumps of greatly varying speeds is available. The speed often quoted, especially by the manufacturers, is the **free air displacement**. This is the speed at atmospheric pressure. It is greater


INTAKE PORT
DISCHARGE VALVE
VANE
ROTOR
STATOR
OIL

Rotary piston pump. Type (*a*) is a single-vane Cenco-Hyvac model. Oil-sealed

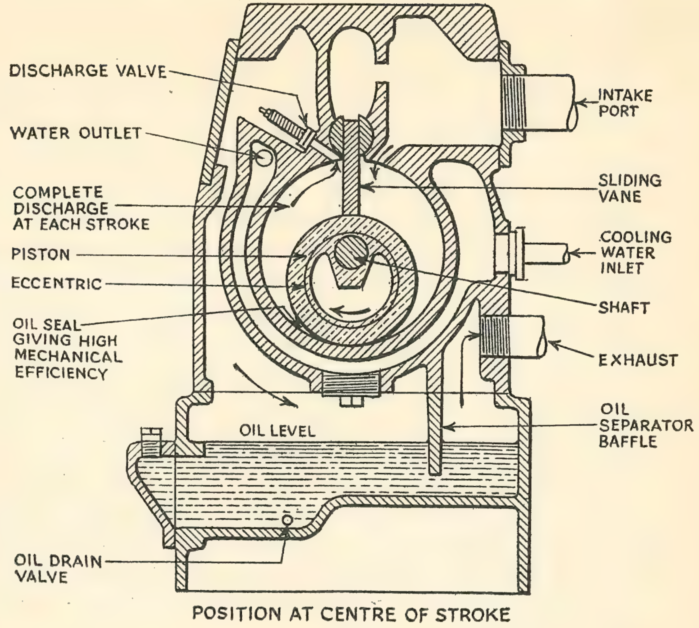
(*a*)


AIR VENT.
OIL SPRAY ARRESTER
INTAKE PORT
FILTER
OIL FILLING PLUG
PRESSURE DRAIN PLUG
OIL LEVEL SIGHT GLASS
DISCHARGE VALVE
PRESSURE DRAIN TUBE.
GRAVITY DRAIN PLUG.
STATOR
ROTOR
VANE

Rotary piston pump. Type (*b*) has two vanes in a diametral slot in the rotor, like the original Gaede pattern (the model shown is a typical Edwards 'Speedivac' pump). Oil-sealed

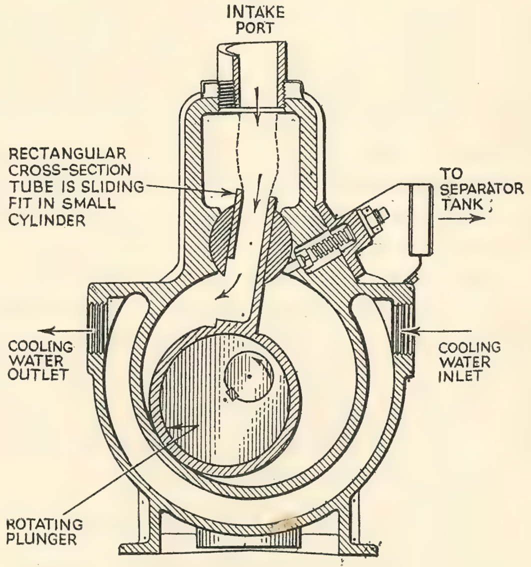
(*b*)

FIG. 2.1 Types of mechanical rotary pump
(Diagrams are cross-sectional views in vertical plane)


DISCHARGE VALVE
WATER OUTLET
COMPLETE DISCHARGE AT EACH STROKE
PISTON
ECCENTRIC
OIL SEAL GIVING HIGH MECHANICAL EFFICIENCY
OIL LEVEL
OIL DRAIN VALVE
INTAKE PORT
SLIDING VANE
COOLING WATER INLET
SHAFT
EXHAUST
OIL SEPARATOR BAFFLE
POSITION AT CENTRE OF STROKE

Rotary piston pump. A Stokes 'Microvac' pump. Oil-sealed

(*c*)


INTAKE PORT
RECTANGULAR CROSS-SECTION TUBE IS SLIDING FIT IN SMALL CYLINDER
TO SEPARATOR TANK
COOLING WATER OUTLET
COOLING WATER INLET
ROTATING PLUNGER

Rotating-plunger pump of the Kinney type. Oil-sealed

(*d*)

FIG. 2.1(*contd.*) Types of mechanical rotary pump
(Diagrams are cross-sectional views in vertical plane)

than the speed at pressures below atmospheric. This figure is sometimes misleading because two pumps of similar overall physical dimensions and with the same speed of rotation in r.p.m., but where one is a single-stage and the other a two-stage pump, can have the same free air displacement but quite different speeds at, say, 10^{-2} torr. Indeed, at 5×10^{-3} torr, the two-stage pump will still have significant speed whereas the single-stage one will have reached its ultimate pressure where the speed is zero. The characteristic curve of speed against pressure for the pump should hence be consulted (§ 2.2).

At the lower end of the range of commercially available rotary pumps there is, for example, the Edwards 2SC20 pump driven by an $\frac{1}{8}$ h.p. motor and with a free air displacement of 20 litres per min, whilst at the higher end is the Kinney rotary piston pump DVD181420, which has a 40 h.p. motor drive and a free air displacement of 19,866 litres per min (702 cu ft/min). This second pump consists of two stages in parallel because it is difficult to construct a single-rotor and stator arrangement of more than a certain size owing to the precision required of the necessary large machine tools, and also because very large rotors would have to withstand great stresses in operation.

Parallel connection of two identical rotor-stator systems will provide twice the displacement but the same ultimate pressure. Series connection provides the same displacement but greater speeds at low pressures and a lower ultimate pressure.

Mechanical rotary pumps of the larger sizes require an electric motor of about 1 h.p. per displacement of 20 cu ft per min. Pumps of displacement greater than 7 cu ft/min (200 litre/min) usually have an oil-feed from a reservoir above or below the pump, this feed-rate being adjustable to the reservoir after being forced through the discharge line, so that continuous oil circulation with little loss is achieved. Smaller pumps are oil-filled, the whole mechanism being immersed in a metal housing filled with oil. Pumps with displacements greater than about 50 cu ft per min are usually water-jacketed to avoid undue temperature rise in operation. A water flow rate of 1 to 2 gallon per min is adequate.

Speeds of rotation adopted are between 350 r.p.m. and 700 r.p.m., the rotor being driven by a pulley- or gear-connected electric motor. The speed—but not the ultimate pressure obtainable—can be increased by a faster drive because the displacement is approximately proportional to the speed of rotation. Increasing the number of revolutions per minute to a marked extent above the manufacturer's recommendations leads, however, to increased vibration, wear and exhaust fumes.

2.2. Characteristic Curves of Rotary Pumps

The performance of a mechanical rotary pump is assessed from a characteristic curve of speed against pressure. If the pump is to be used as a fore-pump to a vapour-stream pump, then a mass-throughput against pressure characteristic is to be preferred (§ 2.17).

If V is the volume of gas enclosed between the pump rotor and stator which is swept out to the atmosphere at each revolution and f is the number of revolutions of the rotor per unit time, then the apparent speed S_a of the pump would be expected to be constant and given simply by

$$S_a = fV \tag{2.1}$$

where both the speed S_a and the volume V are measured at the pressure prevailing at any instant of time.

The curves plotted for such pumps (Fig. 2.2) do, indeed, show a fairly constant speed which is approximately independent of the pressure at the higher pressures, but this speed falls off noticeably at the lower pressures and becomes zero at the ultimate pressure. This can be considered reasonably satisfactorily from the point of view that there is also a leak of gas into the pump whilst it is operating. This leak, which is different from that in the vessel or caused by evolution of gas or vapour by the vessel, is due to the following factors:

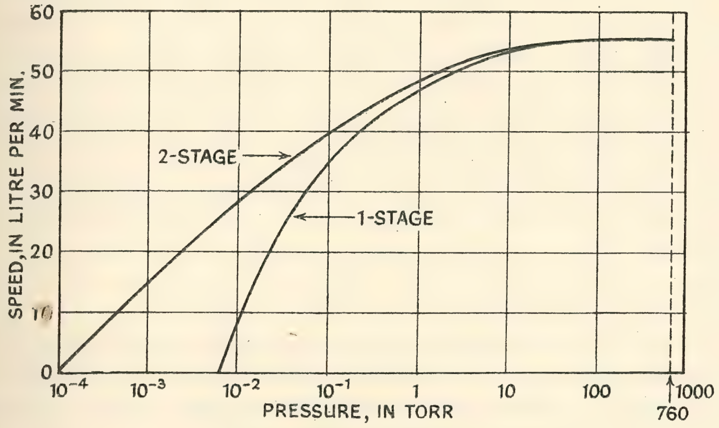


FIG. 2.2 Speed-pressure characteristics of one- and two-stage rotary pumps of medium size

(*i*) The inlet and outlet sections of the pump (Fig. 2.1) are not completely isolated because, first, there is necessarily a finite minimum clearance of the order of 0·002 in. between the rotor and stator walls, and, second, the scraper vane—or equivalent part—is not a perfect fit against the rotor wall.

(*ii*) The residual swept volume between the rotor and stator at each revolution is small but not zero. This is inevitable, first, because the pump would seize up if the fit were too tight; secondly, because the residual swept volume concerned is that at which the outlet valve to air opens against the retarding action of the spring (or other return device) on this valve, to which is added the head of oil plus the atmospheric pressure above it.

(*iii*) These deficiencies are overcome to a considerable extent by the oil with which the pump is filled. However, this oil contains dissolved gases, especially air, has a significant vapour pressure at the working temperature of the pump and probably decomposes to gases and lighter fractions (§ 2.1).

It is interesting to regard these effects as equivalent to a throughput q across the pump (Guthrie and Wakerling, GW1). If q is regarded as constant, the total throughput Q through the working pump at a pressure p is given by

$$Q = S_a p - q \tag{2.2}$$

If the limiting pressure provided by the pump is p_l, it is then proposed to put $q = S_a p_l$. Then equation (2.2) becomes

$$Q = Sp = S_a p - S_a p_l$$

where S is the actual pumping speed. Therefore,

$$S = S_a(1 - p_l/p) \tag{2.3}$$

Such an equation does represent fairly well the type of characteristic obtained. The over-simplifications introduced in this theory are, however, that first the leak rate is due to oil vapour pressure and oil decomposition products as well as dissolved air in the oil and it is not justifiable to express leaks due to the vapour in the simple form employed for the effective air-leak; second, the conductances of the inlet ports to the pump are functions of pressure in the viscous flow region (§ 1.5); thirdly, the outlet valve to air will not operate in an easily predictable manner as a function of the inlet pressure to the pump.

2.3. Failure of Rotary Pumps

The causes of failure of a pump to achieve the pressure and speeds specified by the manufacturer are rarely mechanical defects of the pump itself. However, four causes of failure due to mechanical defects arising after wear—usually after several years of use—are listed below.

(*i*) The outlet valve to air is not functioning properly: it may require adjustment of the screw which determines its travel, or it may be stuck due to inadequate lubrication or because the retarding spring is too weak or broken; in small pumps using spring blades, sometimes retaining a rubber flap valve, this blade is liable to snap after considerable use.

(*ii*) O-rings and other Neoprene seals, if used in the pump construction, may perish or become distorted after many dismantlings.

(*iii*) In the case of some pump types, it is essential to set up the minimum clearance (usually 0·002 in.) between the rotor and stator with a feeler gauge if the pump has been dismantled for cleaning.

(*iv*) Wear of the stator, rotor or vanes. This defect is very unlikely, except after very long use. In practice it sometimes happens that a mechanical pump, after use on a clean, dry system, gives a better ultimate vacuum performance than when new, because the 'fit' of mechanical parts, *e.g.* of the vanes to the rotor walls, is improved and, also, because some of the dissolved air is released from the oil.

The amount of wear, and even abuse, that the mechanical rotary pump will withstand is incredibly high—a tribute to the quality of manufacturers' designs and products. For example, pumps have been known to operate satisfactorily after cleaning even if they have been submerged in sea-water for several days—this did in fact happen occasionally during transit overseas of pumps during the war. Again, pumps have been used with obnoxious chemically active gases like bromine—not a recommended but a sometimes unavoidable procedure—until they have become gummed up and refuse to rotate. On cleaning (and in one case in the authors' experience the vanes had to be cleaned with a light-grade emery paper) the pump will operate satisfactorily with a fresh oil charge added on re-assembly.

Failure to attain the desired ultimate and speed, especially the former, is nearly always due to incorrect usage or maintenance rather than to a defect of the pump itself. **Possible causes of such failures are as follows**: (*i*) leak-to-air in the system or evolution of gas or vapour (especially water vapour) by the system or materials in it. This is the most usual cause of trouble; (*ii*) the oil level is too low, or, in large pumps, the oil feed is not properly adjusted; (*iii*) oil has emulsified with water; it then appears 'cloudy' and as a result, its vapour pressure is too high. It is better to use motor-car oil rather than contaminated vacuum oil, if nothing better is available; (*iv*) the oil is contaminated with volatile liquids, *e.g.* acetone or ether, which have been used for cleaning and not thoroughly removed; (*v*) if strongly reactive agents such as bromine, chlorine, fluorine, sulphur dioxide, hydrochloric acid gas, etc., have been admitted to the pump they will change the oil to a gummy substance which will become deposited on the surfaces of the inner parts of the pump. If deposition is allowed to proceed, the pump will eventually seize up. Chlorinated and fluorinated oils can be used to avoid this to some extent. If possible, a trap for such oxidizing vapours should be inserted at the pump inlet; a cold trap is useful here: (*vi*) inadequate rate of revolution of the pump due to incorrect motor or pulley ratio, or partial motor failure, will lead to reduced pump speed.

Precautions desirable in operating mechanical rotary pumps may be listed as follows: (*i*) for large pumps, especially, ensure that the conductance of the connecting tubing to the vessel, including the effect of orifices of valves, stopcocks and traps, does not impede seriously the pumping speed (*see* § 1.6); (*ii*) use a phosphorus pentoxide trap in the pump line immediately at the pump intake or, alternatively, a cold trap (§ 2.11). Phosphorus pentoxide is strongly hygroscopic (§ 11.3); its use therefore reduces considerably the entry of water vapour to the pump, where the water may emulsify with the oil. The phosphorus pentoxide trap can often be omitted if a gas-ballast pump (§ 2.5) is used; (*iii*) it is difficult to re-start a rotary pump under vacuum; furthermore, if the system is left under vacuum and connected directly to a rotary pump which has been switched off, oil will be sucked out of the pump into the system. It is therefore necessary to isolate the pump from the system by a stopcock or valve before switching off the pump and then admit air to the pump through an air inlet valve (Fig. 2.3); (*iv*) it is advisable to convey the exhaust fumes from a rotary pump via a duct to the outside of the building. This is especially desirable if a large pump—or a number of pumps—are used, not only for the comfort of personnel but also to prevent spoliation of other processed parts, *e.g.* the surfaces of lenses preparatory to 'blooming' (§ 10.9). A vertical outlet duct* is unsatisfactory because water vapour or other condensable vapours that may be pumped will condense on the large cool inner surfaces of the duct. The best practice with large pumps is to include in the outlet duct near the pump a drop-out tank provided with a drain tap; (*v*) a dust filter is often necessary ahead of the mechanical pump to prevent abrasive dust from entering.

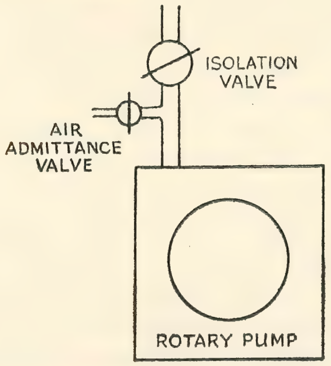


FIG. 2.3 Mechanical rotary pump provided with isolation and air admittance valves

2.4. Removal of Water Vapour by Pumping

A considerable source of difficulty in obtaining vacua is the presence of water vapour in the system. This is especially the case where large metal vacuum tanks are used: the inner walls of such tanks release significant quantities of water vapour on pumping down from atmospheric pressure. Furthermore, in vacuum drying processes (§ 11.1) it may be necessary to remove quite large amounts of water from the tank.

The normal mechanical rotary pump has a limited capacity for pumping water (or other condensable) vapour (Gaede, G1).

Consider a pump with a speed S and a compression ratio C, *i.e.* the ratio of the maximum to the minimum swept volume between the rotor and the stator. Let P_g be the partial pressure of the permanent gas (*e.g.* air) and P_v the partial pressure of water (or other condensable) vapour at the pump inlet. Then

$$C = \frac{P_e}{P_v + P_g} \tag{2.4}$$

where P_e is the ejection pressure required to raise the exhaust valve against the action of its retarding spring plus the pressure of the atmosphere and the head of oil above it. To find the maximum value that P_v can have without condensation of the vapour to liquid during the compression, consider that

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* It is amusing to recall the case of one factory in which the exhaust of the mechanical rotary pumps was correctly conveyed to outside the building but where, unfortunately, the duct was finally in the form of a vertical chimney. Rainwater inevitably got into the rotary pumps. Complaints to the pump manufacturer followed!

CP_v must not exceed P_s, the saturation vapour pressure of water at the temperature of the pump interior. Then,

$$C = \frac{P_s}{P_v} = \frac{P_e}{P_v + P_g}$$

$$\therefore \quad P_v = \frac{P_s P_g}{P_e - P_s} \tag{2.5}$$

For example, for a Kinney pump, the operating temperature—taken to be the temperature of the sealing oil—is 60° C and P_e is 1100 torr. At 60° C, P_s is 150 torr. Therefore,

$$P_v = \frac{150 P_g}{1100\text{–}150} = 0{\cdot}16 P_g.$$

It follows that condensation of water vapour will occur in this pump if the partial pressure of water vapour at the pump inlet exceeds 16% of the ideal gas pressure, *i.e.*, at a total inlet pressure of 1 torr the water vapour pressure must not exceed 0·14 torr.

The most satisfactory remedy is the provision of **gas-ballast** in which air is bled into the region between the rotor and stator during the compression cycle to reduce significantly the possibility of condensation (§ 2.5). Even with gas-ballast provision, the rate at which water (or other condensable) vapour can be removed by a rotary pump is limited compared with the use of a phosphorus pentoxide or a cold trap. The mass of one mole of water vapour is 18 gram and it occupies a volume of 22·4 litre at 760 torr and 0° C. At 60° C (a normal running temperature for a gas-ballast pump) this volume will be 22·4 × 333/273, *i.e.* 27·3 litre. The mass of one litre of water vapour at a pressure of 1 torr is, therefore,

$$\frac{18}{27{\cdot}3 \times 760} = 8{\cdot}7 \times 10^{-4} \text{ gram.}$$

A large rotary gas-ballast pump with a speed of 1000 litre per min is therefore only able to remove 0·87 gram of water per minute at a pressure of 1 torr. This is a particularly significant result with respect to vacuum drying.

On the other hand, a phosphorus pentoxide, activated alumina powder or a cold trap can remove water vapour at a speed which increases with the effective exposed surface area. If every molecule which reaches this surface is considered to be removed from the system, this speed is readily calculated to be 15 litre per sec per cm^2. At a pressure of 1 torr the rate of removal of water vapour is therefore 15 × 8·7 × 10^{-4} gram per sec per cm^2. A trap with an effective surface area of 100 cm^2 therefore removes water vapour at this pressure at a speed of 7·8 gram per min.

2.5. The Gas-ballast Pump

If it is necessary to exhaust a vessel in which volatile liquids (especially water) are present, it is desirable to use either a **gas-ballast pump** or an **oil-stripper unit.** It is now recommended standard practice to use a gas-ballast pump whenever large metal vessels are exhausted. Oil-stripper units (§ 2.6) are preferred if a condensable vapour which reacts with the pump oil is concerned. The use of gas-ballast has become so important that almost all the pump manufacturers now supply pumps with this provision.

The readiness with which the condensation of water vapour occurs in non-ballasted pumps has already been considered in § 2.4. It can only be avoided if the compression ratio C is limited. If free water with a vapour pressure of 17·5 torr at 20° C is present at the pump intake port, a compression ratio C of only 9 : 1—much less than the actual figure—will raise the pressure of the vapour to 150 torr, the saturation vapour pressure at a temperature of 60° C in the pump interior. Water as a liquid will then become mixed with the oil.

In gas-ballast pumps (Gaede, G1) a simple adjustable screw-valve is arranged to admit air from the atmosphere directly into the space between the rotor and the stator at that time in the rotor revolution when compression begins and the swept volume has just been isolated from the pump inlet. This extra air can easily be arranged, by the extent to which the gas-ballast valve is opened, to provide a compressed gas-vapour mixture which reaches the ejection pressure P_e—and so opens the outlet valve—before condensation of the water vapour takes place. The water vapour cannot then condense in the pump; instead, it is discharged to the atmosphere with the air.

The operation of the gas-ballast valve in relation to the rotor cycle is explained by Fig. 2.4 in conjunction with the accompanying legend.

To find the gas-ballast flow required, consider that equation (2.4) will be modified by the contribution of the ballast air to the sum of the pressures P_v and P_g. Suppose this contribution is a pressure P_b. If S_b is the speed at which air is admitted from the atmosphere at a pressure of 760 torr and S is the speed of the pump,

$$P_b = \frac{760S_b}{S}$$

and equation (2.4) becomes

$$C = \frac{P_e}{\dfrac{760S_b}{S} + P_v + P_g}$$

C can attain a maximum value of P_s/P_v, where P_s is the saturation vapour pressure at the pump temperature. Therefore,

$$\frac{P_s}{P_v} = \frac{P_e}{\dfrac{760S_b}{S} + P_v + P_g}$$

$$\therefore \quad S_b = \frac{S}{760}\left(\frac{P_eP_v}{P_s} - P_v - P_g\right) \tag{2.6}$$

and

$$P_v = \frac{P_sP_g}{P_e - P_s} + \frac{760S_bP_s}{S(P_e - P_s)} \tag{2.7}$$

Comparison of equations (2.6) and (2.5) shows that the partial pressure P_v of the water vapour at the inlet can be larger as the gas-ballast flow is increased.

The provision of gas-ballast will obviously increase the ultimate pressure provided by the pump. For a single-stage Leybold pump, model VP2, the ultimate with full gas-ballast is 5 torr and with the gas-ballast valve closed it is 5×10^{-2} torr. However, this disadvantage is unimportant in practice because the gas-ballast valve need usually only be open during the initial stages of pumping when the main bulk of the water vapour is removed. As pumping proceeds, the gas-ballast valve can be screwed in and, finally, closed completely. Indeed, the gas-ballast flow is not provided when S_b is put equal to zero in equation (2.6), *i.e.* when

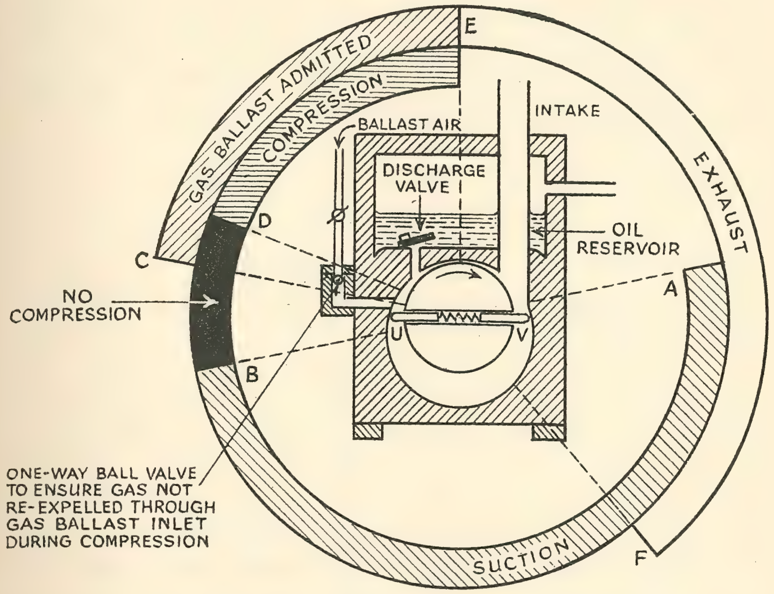

FIG. 2.4 The principle of the gas-ballast pump

V is leading edge of vane. ABCDEF represent successive positions of V during revolution of rotor. When V passes A, space between rotor and stator *below* vane is isolated from intake port; suction occurs from A to B as space *above* vane increases in volume. At B, rear vane U reaches A, then space *above* V becomes isolated from intake port. As V traverses region B to D, the isolated volume of gas in the pump remains constant, *i.e.* there is no compression. Just before D is reached, however, air from the atmosphere enters at position C. As V traverses the region D to E, this air ballast enters the pump as the compression part of the cycle takes place.

$$\frac{P_eP_v}{P_s} - P_v - P_g = 0$$

i.e.

$$P_v \leqslant P_g \bigg/ \left(\frac{P_e}{P_s} - 1\right) \tag{2.8}$$

which, of course, agrees with equation (2.5).

It should be noted that these results assume that the gas-ballast air admitted is dry. Additional ballast will be required if the air has a high relative humidity.

In two-stage mechanical rotary pumps, only the second, *i.e.* backing, stage requires gas-ballast to prevent condensation of vapour in the oil. The ultimate vacuum provided by a two-stage pump is hence not so much affected by full gas-ballast as is the case with a single-stage pump. The Edwards 2SC20 two-stage mechanical rotary pump has an ultimate of 10^{-2} torr with full gas-ballast which is reduced to 10^{-3} torr when the ballast valve is closed.

A further advantage of gas-ballast is that, if the oil does become contaminated with condensable vapours, it can be readily freed of such contamination by simply running the pump with the gas-ballast full on but with the pump isolated by a valve from the system. This clean-up occurs provided that there is no chemical reaction between the vapour and the oil.

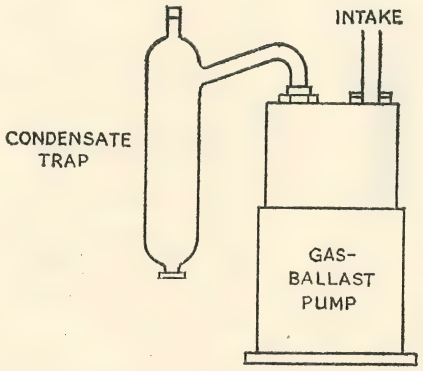

FIG. 2.5 Use of a condensate trap with a gas-ballast pump

A **condensate trap** or **catch-pot** (Fig. 2.5) should be provided in the discharge line to the atmosphere to prevent the condensate from running back into the pump. This precaution is particularly necessary with large gas-ballast pumps.

The gas-ballast pump is particularly suitable for distillation, drying and impregnation processes (Chapters 11, 12 and 13) where appreciable quantities of condensable vapours have to be handled. It is also recommended for large vacuum-coating plants, particularly if materials such as paper and plastics are to be metallized. The provision of gas-ballast is not so important in small-scale glass systems and in, for example, the pumping of electron tubes where condensable vapours are not a source of difficulty.

If large quantities of condensable vapours have to be pumped, a two-stage pump combination with a large gas-ballast pump backed by a smaller model is recommended with a water-cooled **condenser** inserted between the two stages. This condenser (Fig. 2.6 and Plate 1) traps most of the vapour after pre-compression in the first-stage pump. For example, if a water vapour pressure exceeding 1 torr exists at the intake port, this pressure will be increased to 20 torr or more between the two pumps and the vapour will condense to water in the condenser. Leybold's Nachfolger—who were the first manufacturers to put gas-ballast pumps on the market—emphasize in their specifications that the quantity of condensed liquid is often underestimated. Thus, the Leybold S150 gas-ballast pump is able to remove about 2 kg of water vapour per hour of which the condensation to liquid of only a minute fraction within the pump oil will suffice to impair the pump operation.

Gas-ballast operation is less effective if the water vapour entering the pump is at a temperature exceeding 30° C. Water has a vapour pressure of 32 torr at 30° C. If the pump interior is at 60° C, at which temperature the water vapour pressure is 150 torr a compression ratio of only 150/32, *i.e.* 5, will be sufficient to cause condensation of the vapour. Minimum compression ratios of between 6 and 10 are demanded if reasonable pumping speeds are to be maintained. If the vapours from the system are likely to be at temperatures exceeding 30° C, a condenser is recommended in the line to the pump intake (Fig. 2.6).

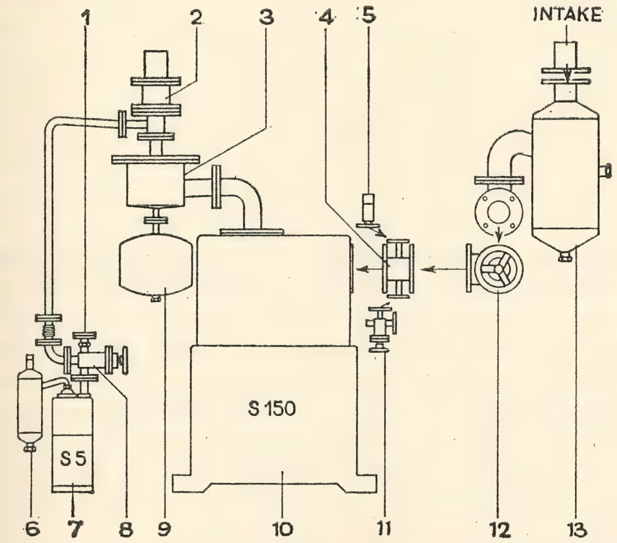

FIG. 2.6 Leybold pump combination S150-S5 with condenser and accessories

1, Flange connectors; 2, safety valve (to guard against excess pressure between pumps); 3, condenser; 4, cross-piece connector; 5, thermocouple gauge; 6, catch-pot on discharge side; 7, fore-pump (displacement: 85 litre per min); 8, isolation valve; 9, receiver for condenser; 10, main pump (displacement: 2500 litre per min); 11, air-inlet valve; 12, right-angle isolation valve; 13, intake-side trap

Power and Kenna (PK1) discuss in detail the vapour pumping characteristics of gas-ballast pumps; they emphasize that a high pump temperature is of very great assistance when pumping vapours, especially oil-soluble vapours.

2.6. Oil-stripper Units

To prevent condensable vapours from spoiling the rotary pump oil, an oil-stripper unit can be used. In this case, the oil is discharged from the pump, passed through an oil-refiner unit and then re-circulated to the pump. As a principle, this is less satisfactory than the use of gas-ballast because additional, costly, cumbersome apparatus is required and the vapour is not prevented from liquefying. The oil-stripper is necessary, however, if the vapour present reacts with the pump oil to form resinous compounds; even so, it is not an entirely satisfactory arrangement because some contamination of the pump oil and even of the working surfaces is still possible. In fact, unless pressures below 0·5 torr are mandatory, it is often better to use steam-ejector pumps (§ 2.18) for large quantities of reactive vapours.

In the refiner, or 'stripper', the oil is cleaned of vapours by steam or electric heating, centrifuging or passage through a filter, *e.g.* of kieselguhr. Solvents in oil cannot be removed simply by heating unless the oil is raised to its boiling point; this is forbidden because the oil would decompose. Pfeiffer of Wetzlar (Germany) provide a pump with an attached unit in which a fraction of the contaminated oil is removed and a corresponding amount of fresh, clean oil is restored. F. J. Stokes (U.S.A.) describe an 'oil clarifier unit' which employs a filter through which the oil is circulated. The same company also markets an 'oil devaporizer' which continuously purifies the oil by distilling water off as steam. Associated Electrical Industries (Manchester, England) supply an oil-stripper unit which cleanses the oil of volatile vapours by electric heating. A small, gear-type pump, operated by a $\frac{1}{4}$ h.p. motor, is used to extract the contaminated oil from the pump. The oil is circulated by this pump around a heat exchanger coil and up a central pipe to the top of an evaporator. It then flows down the inside of a baffle tube and up the annular space between this tube and the evaporator tube, being heated on the way. At the top of the evaporator tube, the oil spills over and falls in the form of a thin film down the outside, to be collected in a reservoir. In the evaporator, the temperature of the oil is thermostatically controlled to a maximum of 120° C, and, as it flows down the outside of the tube in a thin film, the contaminants are evaporated off, to be condensed on the inside surface of the condenser tube, and then run down to the collecting trough where they are passed out of the system by the attached drain-pipe. The hot, cleaned oil which has collected in the reservoir is cooled by the incoming oil from the pump before being re-circulated via the outlet. This plant can handle 15 gallons of contaminated oil per hour and 4 gallons of water per hour are necessary for condenser cooling. The heater element is rated at 2·5 kW.

Holland (H1) recommends an aeration method which is especially suitable for pumps (*e.g.* of the Kinney type), in which the oil is in a separate reservoir and is fed to the pump through connecting pipe lines. Volatile constituents are removed by bubbling air through the oil which is maintained at about 90° C.

2.7. The Roots Blower

In 1867 (Glazebrook, G2) Elihu Root exhibited at the Paris Exhibition an air blower with a mechanical efficiency of about 75%. This type of blower has recently been adopted for the transport of large quantities of gas through a vacuum system.

The Roots pump—as it is preferably called in its new application—is of great value in large-scale vacuum plant where very large quantities of gas in the pressure region between 10^{-3} and 1 torr have to be handled. Processes in which such a demand is encountered are the drying of electric capacitors and cables (Chapter 12), vacuum distillation (Chapter 13), freeze-drying (Chapter 11), vacuum metallurgy (Chapter 14) and, in particular, steel degassing. In some large modern plants as much as 10,000 m^3 per hour (167,000 litre per min) of gas or vapour must be pumped away. Several large mechanical rotary pumps in parallel would be needed to provide this speed; the Roots pump is now available as a single unit with speeds of 10,000 m^3 per hour or more (Nöller and Thees, NT1).

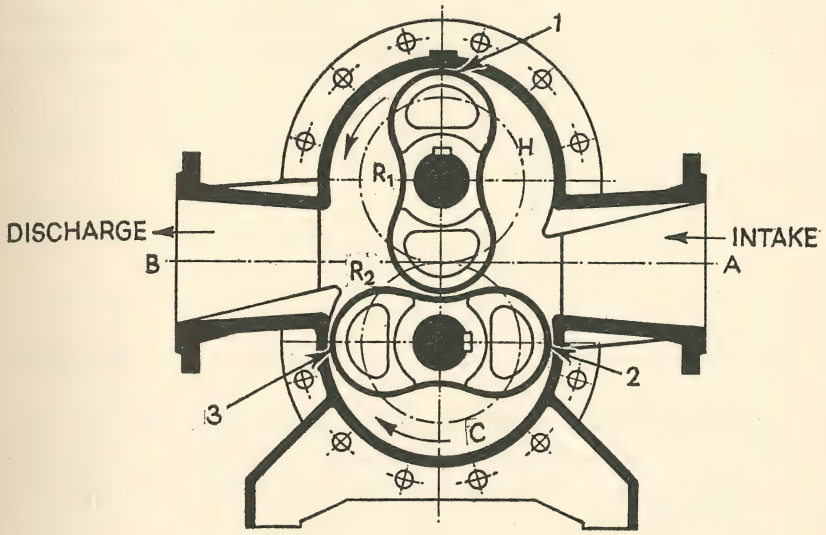

FIG. 2.7 Principle of the Roots pump (vertical cross-section)

The Roots pump (Fig. 2.7) consists of two steel rollers or impellers R_1 and R_2 each with a 'figure-of-eight' cross-section. These are rotated in opposite directions within the pump housing. If the direction of rotation is as shown by the arrow in Fig. 2.7, air will be sucked in at A and delivered through B. The impellers have identical cross-sections and are dimensioned and arranged so that some part of the surface of R_1 is a close fit to a part of the surface of R_2 throughout the rotation. These impellers are also a close fit inside the pump housing H, *i.e.* there is a small clearance (about 0·1 mm) at the points 1, 2 and 3 at the instant in the revolution illustrated by Fig. 2.7; as point 1 moves around the inside wall of the pump housing, points 2 and 3 move correspondingly. The rotating impellers do not, however, touch one another, nor do they touch the housing. Hence, the inlet port A is isolated, in effect, from the outlet B except for a narrow slit.

On rotation, air from the inlet port A is first trapped within the space C between the roller R_2 and the pump housing and is then subsequently expelled through the discharge outlet B. Air will also stream from B back towards the inlet port; on further rotation, however, this air will also be returned to the discharge at *B* together with the air conveyed from the tank connected to the inlet *A*. This process takes place with both rollers R_1 and R_2. On account of the back-streaming air, the efficiency of the compression process in Roots pumps is lower than that for mechanical rotary pumps provided with a discharge valve. However, high speeds of pumping are possible because the speeds of rotation (2000 to 3000 r.p.m. for small Roots pumps and 1000 to 2000 r.p.m. for larger models) can be much higher than in the usual mechanical rotary pump because the rotating parts do not touch one another. No sealing oil is used.

Nöller and Thees (NT1) discuss the working of a Roots pump in comparison with a mechanical rotary pump of the usual design by reference to a pressure-volume chart (Fig. 2.8). In the Roots pump the work done in compressing the gas is given by the area of the almost rectangular figure *abcd*. For a pump with an outlet discharge valve, in which adiabatic compression of the gas takes place, the figure of smaller area *abed* is concerned. Nevertheless, for ratios of the discharge pressure p_d to the intake pressure p_i of about 10 : 1 (shown by calculation and practice to be the most favourable operating condition, Thees, T1) the Roots pump is essentially more efficient because of freedom from friction.

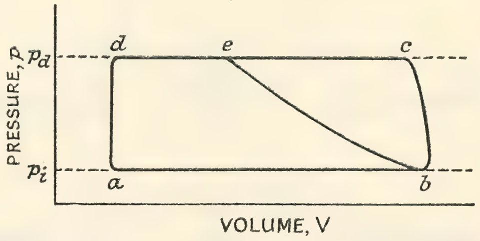

FIG. 2.8 Pressure-volume charts for a rotary pump and for a Roots pump

The Roots pump has a theoretical speed S_T given by the product of the volume of trapped gas within the created space *C* and the number of revolutions per sec. However, this speed is reduced by the gas that streams back from the discharge side to the inlet side. Volumetric efficiency η is therefore defined as

$$\eta = S/S_T$$

where *S* is the actual speed.

The rate at which gas will stream backwards in the unwanted direction increases with the compression ratio p_d/p_i and with the conductance to gas flow of the effective slit provided by the separations between the rollers and between the rollers and the pump housing. This conductance will be less at lower pressures. It is therefore only possible to obtain ratios of p_d/p_i of about 3·5 if the discharge is to the atmosphere, *i.e.* p_d is at 760 torr; p_i can then only be about 200 torr. The discharge pressure p_d is therefore best in the region of 1 torr which can be provided by a mechanical rotary pump used as a fore-pump to a Roots blower. A volumetric efficiency of about 0·8 is only achievable if the pump is used as a compressor from 1 atm at the inlet to 2 atm at the outlet, *i.e.* $\frac{p_d}{p_i} = 2$; this ratio $\frac{p_d}{p_i}$ can be as much as 10 under rough vacuum conditions.

The throughput of gas provided by the Roots pump will be p_iS. This throughput must also be handled by the fore-pump. If the fore-pump has a speed S_F at the Roots pump discharge pressure p_F, then

$$p_iS = p_dS_F$$

As $\frac{p_d}{p_i}$ can be 10 for the Roots pump, the fore-pump need only have 10% of the speed of the Roots pump. The usual single-stage mechanical rotary pump has a speed which is approximately constant over the pressure range from 760 torr to 0·1 torr (*see* Fig. 2.2), so it serves very well as a fore-pump to the Roots pump for widely varying values of p_i.

Nöller and Thees (NT1) give the pressure-speed characteristic *A* (Fig. 2.9) for a Roots pump operating with a matched single-stage gas-ballast pump as fore-pump compared with the characteristic *B* of the gas-ballast pump alone. The gas-ballast pump speed S_F is practically constant from atmospheric pressure down to 0·1 torr where it begins to decrease to reach zero at a pressure of 2×10^{-3} torr. The speed *S* of the Roots pump combined with the gas-ballast pump is not much larger than that of the fore-pump alone at pressures above 100 torr, but is several times greater for pressures below 10 torr and does not fall to zero until an ultimate of 3×10^{-4} torr. The maximum speed of the Roots pump is at a pressure of 5×10^{-2} torr, where the speed of the combination is about 30 times that of the fore-pump alone.

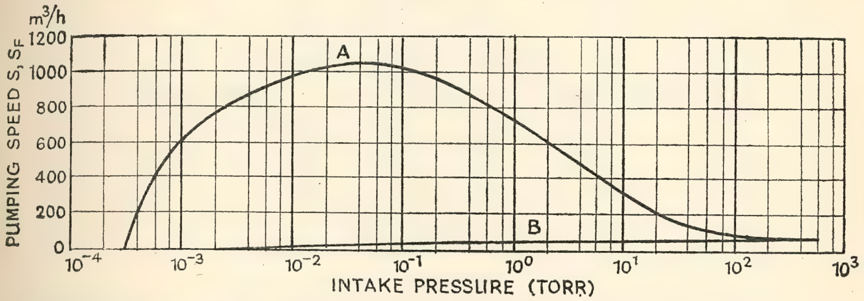

FIG. 2.9 Dependence of the speed of a Roots pump on the intake pressure when a gas-ballast pump is used as a fore-pump

If a condensable vapour is being pumped, a condenser trap must be used between the Roots pump and the fore-pump. This is because the Roots pump will only operate efficiently with compression ratios of not more than 10 : 1; the inlet pressure p_i cannot therefore be less than about 0·1 p_v, where p_v is the saturation vapour pressure of the condensate. If the condensate is water, and the trap is water-cooled to be at a temperature of 20° C, p_v is 17 torr and p_i cannot be less than 1·7 torr. If the trap is cooled below room temperature, p_i can then be less.

Two-stage Roots pumps are also available in the smaller sizes whilst two single-stage Roots pumps in series can be used if larger pumps are necessary. Each stage can provide a pressure ratio p_i/p_a of 10, giving 100 together. The ultimate pressure is then limited primarily by the vapour pressure of the film of oil from the fore-pump which collects on the interior of the Roots pump during operation. Two-stage Roots pumps with a gas-ballast fore-pump can provide an ultimate total pressure of about 2×10^{-4} torr and an ultimate permanent gas pressure of about 5×10^{-6} torr.

A difficulty with Roots pumps—which contain no oil filling—is to convey away the heat produced during compression of the gas. This heat can only escape by radiation and conduction across the clearances between the rollers and the housing. If the heat developed is too great, thermal expansion might result in the pump seizing up. The simplest way of limiting this heat production is by reducing the amount of air conveyed through the Roots pump by pumping during the initial stage of evacuation with the fore-pump alone until the pressure in the vacuum tank is reduced from atmospheric to about 2 torr. The Roots pump is then set in operation. Since the high speed of pumping is only required at the lower pressures when the vacuum process itself (*e.g.* metal degassing) is commenced, it does not usually matter that this initial production of a rough vacuum will take longer. The Roots pump is switched on later and connected in the vacuum circuit by a suitable simple arrangement of isolation valves or, alternatively, is left in circuit without driving power during the initial pumping; the air pumped through it will then simply rotate the rollers slowly, but, of course, the presence of the idle Roots pump will introduce a considerable impedance to gas flow to the fore-pump. The power to rotate the Roots pump can be supplied at a suitable time by a pressure-operated switch.

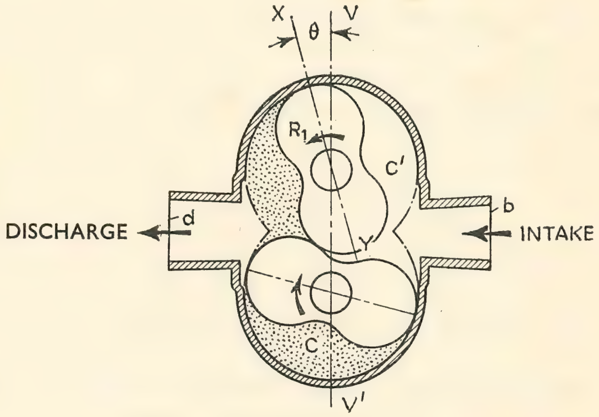

FIG. 2.10 Air in the fore-vacuum region of the Roots pump; the fore-vacuum space swept by the impellers during rotation is denoted by dots (*after Nöller and Thees*, NT1)

Other ways of limiting the production of heat are: (*i*) to reduce the speed of rotation of the Roots pump during the initial stages of evacuation when large masses of air have to be drawn through the system; (*ii*) to provide a by-pass tube across the Roots pump which is closed by a pressure-operated isolation valve when the pressure has been reduced to about 2 torr. In practice, the first procedure is used for pumps with speeds of 5000 m³ per hr or more, and the second for smaller pumps. Using procedure (*i*) an electronically controlled d.c. driving motor is used, of which the speed of revolution is automatically adjusted by the gas pressure.

The permissible maximum pressure at which the Roots pump can be operated without over-heating can be raised to 20 torr or even 80 torr by cooling the rollers. To study methods of doing this (Nöller and Thees, NT1) consider Fig. 2.10. Let θ be the angle through which the axis XY of roller R_1 has turned in the direction of the arrow from the vertical VV'. As θ increases from zero on rotation of the rollers, the trapped volume of gas within the space C is suddenly released to the fore-vacuum region. Since the fore-vacuum pressure is greater than the intake pressure to the Roots pump, gas streams in the opposite direction to the pumping direction, but this gas is returned to the fore-vacuum on further rotation. During this process, the air increases in temperature and heats up the pump rollers and housing. When θ reaches 90°, the initial volume of the fore-vacuum is restored. On further rotation, the trapped gas in C' is released to the fore-vacuum, and so on.

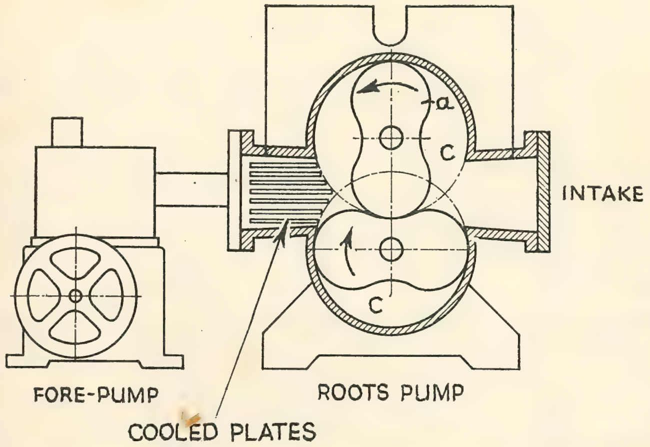

FIG. 2.11 Arrangement of cooled plates in the discharge port to the fore-pump

To reduce this heating effect, water-cooled metal plates are arranged parallel to the axles of the impellers in the discharge port to the fore-vacuum (Fig. 2.11). The air which streams into the space C when it is suddenly opened to the fore-vacuum at a specific time in the revolution cycle must then pass over these cooled plates and so reduce the pump interior temperature.

If it is required to operate a Roots pump with pressure differences between the inlet and outlet of more than 80 torr, without reducing considerably the roller clearances, oil-cooled rollers must be used. The rollers then have hollow axles through which cooled oil is circulated from an auxiliary oil-pump. This cooled oil must also be circulated through a jacket around the pump housing, otherwise too great a temperature difference will exist between the cooled rollers and the housing. The useful range of inlet pressures for large oil-cooled Roots pumps is 10^{-3} to 20 torr.

Efficient operation of the Roots pump in the intermediate vacuum region between those pressures at which the vapour pump and the mechanical rotary pump have their maximum speeds is indicated in the graphs of Fig. 2.12.

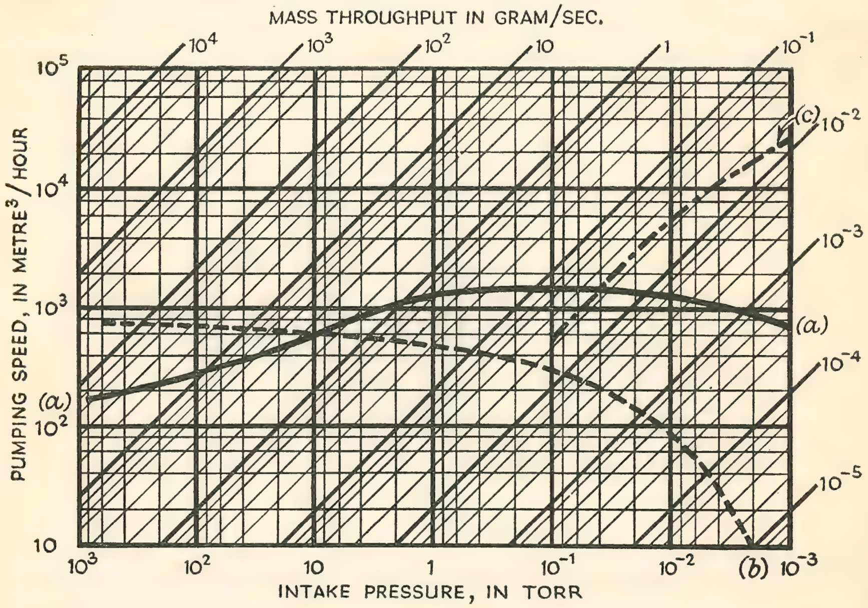

FIG. 2.12 Dependence of the speed and the mass-throughput* of a Roots pump on the intake pressure

Curve (*a*) for Roots pump of speed 1500 m³/h at 4×10^{-2} torr with gas-ballast fore-pump of speed 180 m³/h; curve (*b*) for a two-stage gas-ballast pump with a displacement of 720 m³/h; curve (*c*) for an oil vapour pump with a speed of 6500 litre per sec at 10^{-3} torr

A wide range of sizes of Roots pump is now available. The small two-stage Leybold Ruvac Z05 (overall dimensions without built-on electric motor are approx 30 × 30 × 38 cm) has a maximum speed of 70 m³ per hr (1162 litre per min) and provides an ultimate total pressure of 2×10^{-4} torr. The largest models at present have maximum speeds of 20,000 m³ per hr (332,000 litre per min) and an ultimate total pressure of 10^{-3} torr. The pressure range from 10^{-3} to 20 torr is their appropriate field of application.

2.8. Vapour Pumps

There are two main types of pump which employ vapour issuing from a jet as a means of pumping. They are **diffusion** pumps and **ejector** pumps. Both

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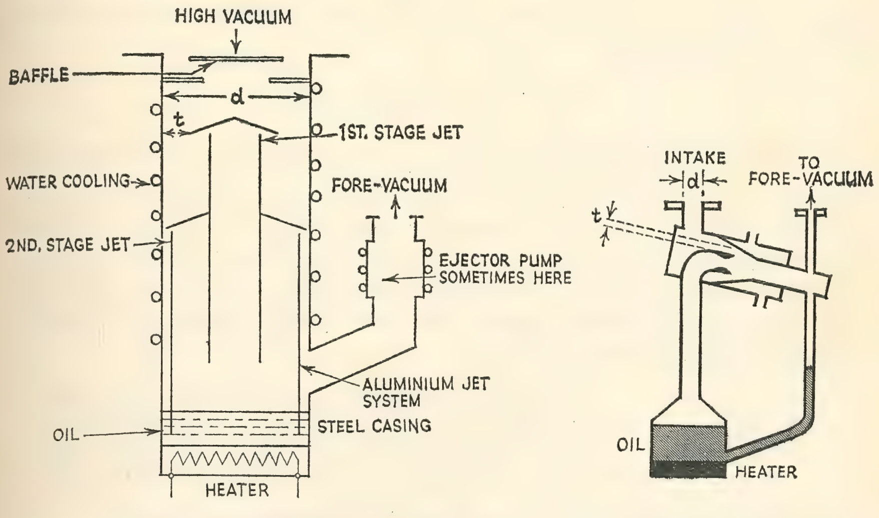
* *See* § 2.17 for detailed explanation of mass-throughput.

types work relative to a fore-pressure provided, usually by a mechanical rotary pump. Vapour pumps employ either mercury or a low-vapour pressure oil as a pump fluid. Diffusion pumps, whether they employ mercury or oil, operate with boiler pressures of usually not more than 5 torr (higher figures are sometimes encountered in small mercury pumps); they pump gas at intake pressures in the range from 10^{-7} to about 2×10^{-2} torr and discharge this gas, after compression by the vapour stream, to a fore-pressure of usually not more than 5×10^{-1} torr for a single-stage pump. Ejector pumps, on the other hand, are designed to have maximum speeds at an intake pressure of 10^{-2} torr or more and operate with fore-pressures greater than 5×10^{-1} torr. Combinations of the diffusion and ejector principles are encountered in **diffusion-ejector pumps.** In these the first-stage jet (that nearest to the intake, *i.e.* fine-side port) operates as a diffusion jet whereas the second (or sometimes the third) and other jets operate as ejectors.



(*a*) VAPOUR DIFFUSION PUMP (*b*) VAPOUR EJECTOR PUMP

FIG. 2.13 Working principle of vapour stream pumps of the diffusion and ejector patterns

This broad classification does not indicate the difference in working principle between the diffusion and ejector methods. This distinction is described more fundamentally by considering the mean free path of the gas molecules at the intake port (*i.e.* mouth) of the pump in relation to the throat width (*i.e.* nozzle clearance), (Fig. 2.13). If the mean free path λ is greater than the throat width t, the diffusion principle applies and the pump fluid (mercury or oil) issues from the jet in a freely expanding stream which is directed by the jet disposition and design towards the fore-vacuum region. The molecules of the vapour stream collide with the gas molecules entering through the intake port and give them velocity components towards the fore-pressure region, so that a pressure gradient is established between the fine and fore vacuum sides.

The vapour stream is not essentially influenced by the gas pumped. In the ejector pump, on the other hand, λ may be significantly less than t, and the intake gas is entrained within the inter-molecular collisions of the now denser vapour stream, resulting in viscous drag and turbulent mixing which carries the gas at initially supersonic speeds down a pump chamber of diminishing cross-section and through an orifice near the fore-pressure discharge region (Jaeckel, Nöller and Kutscher, JNK1).

2.9. Diffusion Pumps

Consider the order of size of the intake port diameter if a diffusion pump of a given speed is required. Suppose the internal diameter of the intake port is d cm and the throat width is t cm, *i.e.* $(d - t)$ cm is the diameter of the jet arrangement (Fig. 2.13(*a*)). The area A of the intake annulus which forms the pump throat is given by:

$$A = \frac{\pi d^2}{4} - \frac{\pi(d-t)^2}{4}.$$

In accordance with equation (1.12) it is impossible for a gas of molecular weight M to pass through this area at a speed exceeding $62{\cdot}5A/\sqrt{M}$ litre/sec, which is $11{\cdot}6A$ litre/sec for air. It can be shown (Dayton, D2) that, in theory, the entrainment of gas molecules by the vapour stream cannot achieve an efficiency of more than 50%. In practice, efficiencies of some 30 to 45% are obtained in well-designed pumps. This leads to the definition of the **Ho coefficient** or **speed factor** as follows:

$$Ho \text{ coefficient} = H = \frac{\text{the admittance, } i.e. \text{ the true forward pumping speed across the throat of a vapour pump}}{\text{the maximum flow rate through the throat area as evaluated from the molecular effusion law}}.$$

The admittance, *i.e.* true pumping speed S, is therefore given by

$$S = \frac{62{\cdot}5\pi H}{4\sqrt{M}}\left[d^2 - (d-t)^2\right] \text{ litre/sec} \qquad (2.9)$$

For air,

$$S = \frac{11{\cdot}6\pi H}{4}\left[d^2 - (d-t)^2\right] \text{ litre/sec} \qquad (2.10)$$

Put $H = 0{\cdot}4$, which is the maximum achieved in practice, then, for air,

$$S = 1{\cdot}16\pi\,[d^2 - (d-t)^2] \qquad (2.11)$$

If $t = d/3$, say, in a practical case of a large diffusion pump,

$$S = 1{\cdot}16\pi\left[d^2 - \left(\frac{2d}{3}\right)^2\right] = 2d^2 \text{ approx} \qquad (2.12)$$

a simple, easily remembered result.

A pump with an admittance S of 1000 litre/sec would hence need to have an inlet port diameter d given by

$$d = \sqrt{\frac{1000}{2}} = 22{\cdot}4 \text{ cm} = 9 \text{ in.}$$

This is about the diameter encountered in diffusion pumps of such speed.

A wide range of sizes of oil-diffusion pumps are available with inlet port diameters from 1 in. to 24 in. or more in Britain and Germany and up to 36 in. in America; and with corresponding speeds (unbaffled) from about 10 litre/sec for the 1 in. type up to 12,000 litre/sec for the 24 in. pump. The ultimate pressure provided is somewhat better than 5×10^{-6} torr, but this depends on the prevailing conditions in the system, the type of diffusion pump and the oil used. Indeed, ultimates of 10^{-7} torr can be achieved and 10^{-9} torr is claimed for some designs (§ 2.14).

Figure 2.14 illustrates two typical oil diffusion pumps: (*a*) is a glass single-stage pump (Consolidated Electrodynamics Corporation) which provides an ultimate vacuum of 10^{-5} torr with a maximum backing pressure of 8×10^{-2} torr; (*b*) is the Edwards High Vacuum Ltd. Type 903B, which has an unbaffled speed of 1500 litre/sec and provides an ultimate vacuum of 5×10^{-6} torr or lower. Fig. 2.15 shows a glass mercury diffusion pump (Ishii and Ito, II1) which can be constructed by a skilled glass-blower and which provides an ultimate vacuum of less than 10^{-6} torr, provided that a liquid-air trap is used.

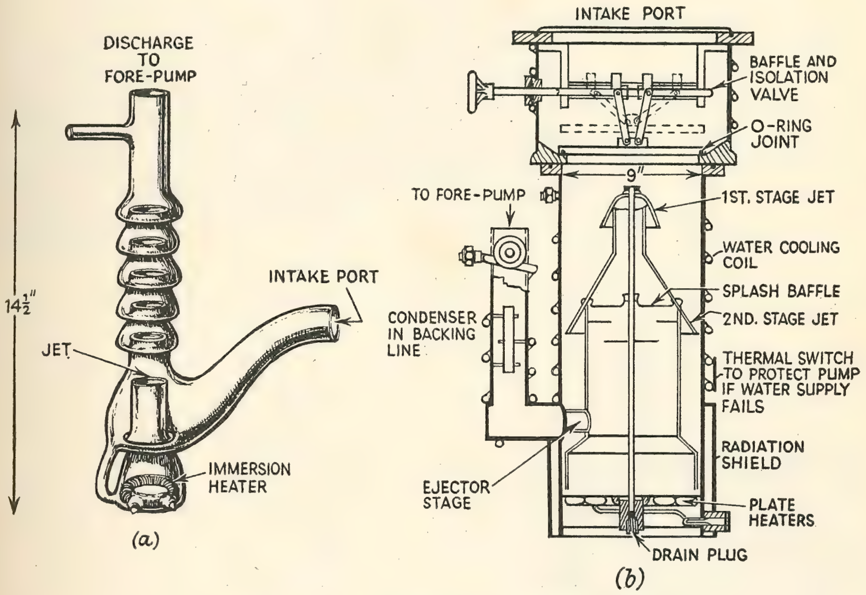
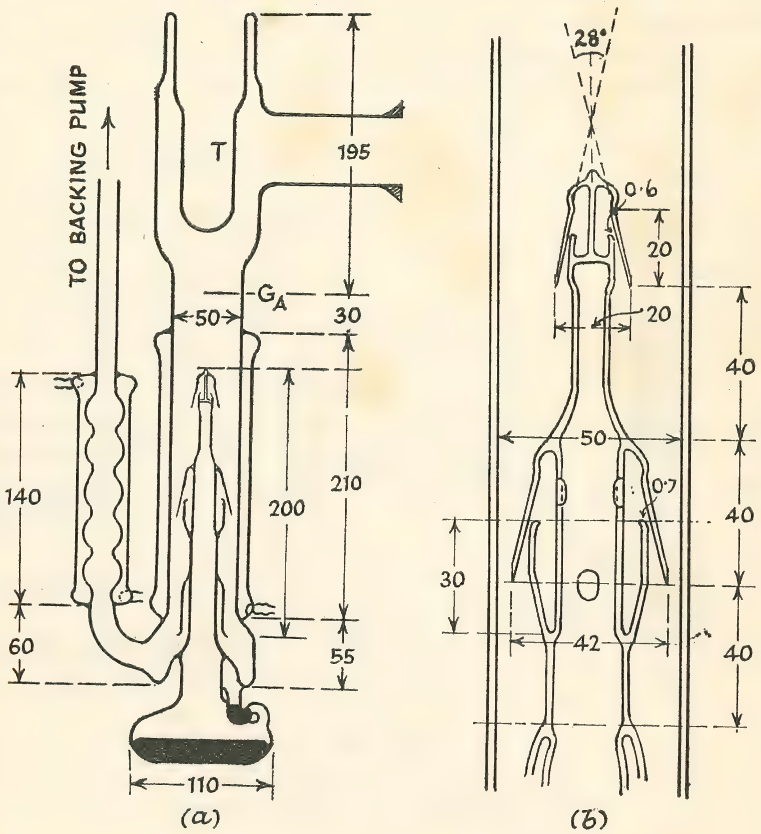


FIG. 2.14

(*a*) A small glass oil diffusion pump
(*b*) A typical large oil diffusion pump

Until quite recently mercury diffusion pumps have not been made in such large sizes as oil diffusion pumps; this has no doubt been due to the necessity for using a liquid-air filled or refrigerated cold trap to enable the lowest total pressures of rather less than 10^{-6} torr to be attained. There is now, however, a considerable revival of interest in the design of large mercury diffusion pumps, particularly for large-scale ion accelerators (*e.g.* the synchro-cyclotron and the proton-synchrotron) used in nuclear physics where the back-streaming of oil (§ 2.10) from oil diffusion pumps has proved to be troublesome.

Smith (S3) lists the large mercury diffusion pumps available; they range from the Edward High Vacuum Ltd. Type 6M3 with an intake diameter of 10 in. and a speed (with cold trap and baffle) of 250 litre/sec, to the Consolidated Electrodynamics Corporation MHG—10000 with an intake diameter of 32 in. and a speed (with cold trap and baffle) of 3500 litre/sec. (Fig. 2.19). Both these pumps provide an ultimate pressure (with cold trap) of 10^{-7} torr.



(*a*) (*b*)

FIG. 2.15 A glass mercury diffusion pump (*dimensions in mm*)

T, cold trap; pumping speed at G_A = 30 litre per sec

For details of manufacturers of mercury and oil-vapour pumps see Appendix D. Air-cooled pumps of the smaller sizes (Plate 2) as well as water-cooled diffusion pumps are available from some firms.

2.10. Back-streaming and Back-migration; Baffles

Vapour pumps suffer from two defects whereby the pump fluid enters the vacuum tank. The first of these is **back-streaming.** This phenomenon is due

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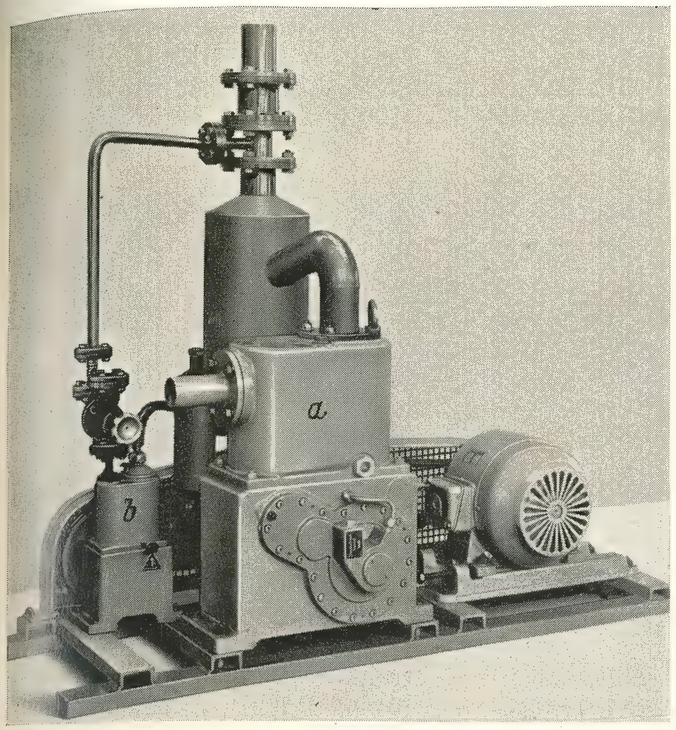


Courtesy of E. Leybold's Nachfolger

Plate 1

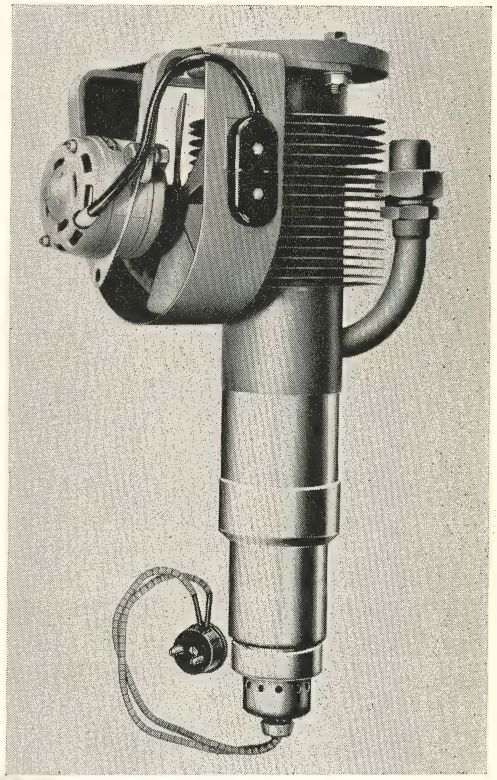
Pump combination with condenser and accessories

The large rotary gas-ballast pump *a* (displacement: 60 m^3 per hour) is backed by a smaller gas-ballast pump *b* (displacement: 6 m^3 per hr). Between the pumps is an inter-stage condenser. This traps most of the vapours after compression in the larger pump. It is particularly useful for intake water-vapour pressures exceeding 1 torr, because, then, the vapour pressure after compression is at least 20 torr and the water condenses out in this water-cooled condenser. For lower water-vapour pressures at the intake, a simpler inter-stage trap suffices. A release valve fitted on the backing side of the larger pump guards against a build-up of pressure exceeding 760 torr between the stages (*see* p. 40).

Plate 2

Air-cooled oil diffusion pump, Metrovac Type A03B

Pumping speed (dry air): 55 litres per sec below 10^{-3} torr (pump unbaffled: pressure measurement with hot-cathode ionization gauge). Ultimate pressure: 10^{-6} torr using Apiezon B oil; highest permissible backing pressure: $3{\cdot}5 \times 10^{-3}$ torr at a heater loading of 500 watts (*see* p. 52).



Courtesy of Instrumentation Division of Associated Electrical Industries (Manchester) Ltd.

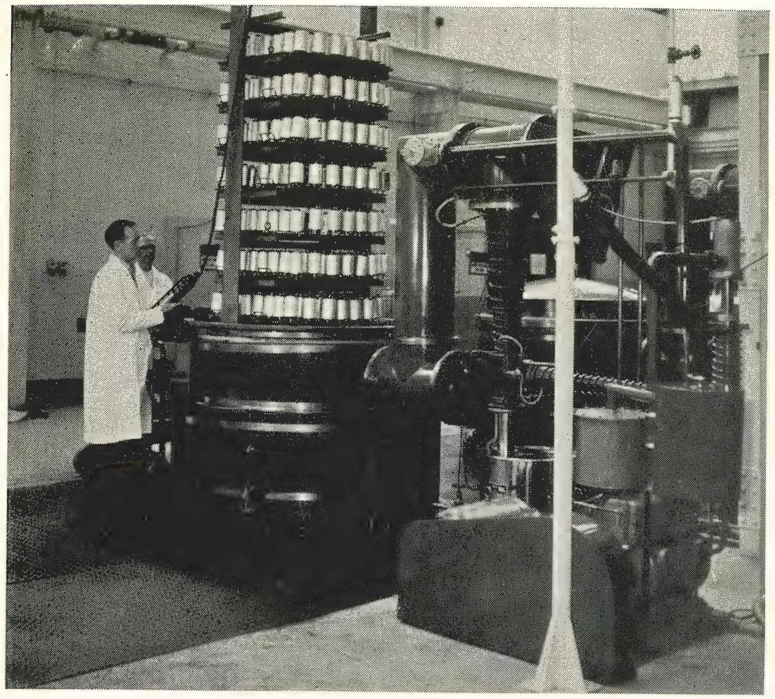


Plate 3

An 18B3 oil vapour ejector pump (Edwards High Vacuum Ltd.) in use in conjunction with a rotary backing pump for the evacuation of plant for the vacuum impregnation of power capacitor elements (*see* p. 79).

Courtesy of Messrs. Johnson and Philips Ltd., and Edwards High Vacuum Ltd.

Plate 5

An evapor-ion pump, type E1–2000

Intake port internal dia.: $11\frac{3}{16}$ in.; creates a 'dry' vacuum in range 10^{-8} to 10^{-4} torr. Pumping speeds are a maximum at about 2×10^{-6} torr; for nitrogen this maximum speed is 1900 litres per sec; for oxygen, 1000 litres per sec and for hydrogen, 3000 litres per sec (*see* p. 305).

Courtesy of Consolidated Electrodynamics Corp.

to a small fraction of the molecules of the working fluid (oil or mercury) travelling from the first stage jet in the wrong direction *i.e.* towards the fine-side region instead of towards the fore-vacuum space. This undesired direction of travel is either imparted to the molecules initially as they issue from the jet, or, more likely, it is acquired after impacts with gas molecules or with other vapour molecules in the stream. To this is added the effect of evaporation of pump fluid from the nozzle itself. Thus it is evidence of unsatisfactory design if this nozzle is wet, *i.e.* oil films cling to it during pumping.

The second defect is **back-migration.** This is due to re-evaporation of the working fluid from baffles, the walls of the pump and the connecting tube to the vessel.

The term **back-diffusion** is frequently used erroneously to denote these phenomena. Back-diffusion is a quite distinct process which results in loss of pumping speed and ultimate vacuum due to the passage of gas or vapour (*not* the pump fluid vapour) from the fore-vacuum to the fine-side region.

Back-streaming of the working fluid into the vessel can be largely avoided by the use of a **baffle.** It can be reduced by suitable design of the pump jet arrangement and is usually less in diffusion pumps of the self-fractionating and self-purifying types (§ 2.14).

Methods of measuring back-streaming rates are described by Power and Crawley (PC1). The usual procedure is to arrange a collector plate above the mouth of the pump and weigh the amount of pumping fluid collected in a measured time. These authors emphasize that this collector plate should be water-cooled by the water flow on its way to the pump jacket cooling coil or jacket. The true back-streaming rate is then determined since the collector plate is thereby as near as possible to the ambient temperature in the test dome placed over the pump mouth.

Back-streaming is influenced greatly by the pump design (see Power and Crawley for a full-account, PC1) the following factors being important (Latham *et al.*, LPD1): the length of the cooled pump walls above the top jet; the design of the jet assembly and especially the diameter of the jet cap; the boiler pressure; the degree of fractionation or self-purification (§ 2.14). Latham *et al.* showed experimentally that the rate of back-streaming plus migration encountered in an Edwards High Vacuum Ltd. Speedivac 203 oil-diffusion pump ($2\frac{1}{4}$ in.-dia. intake port) varies little with the type of oil used (Octoil-S, DC 702 and DC 703 were studied, see Table 2.2) for a given heater input to the pump boiler, if the rate is quoted in molecules/min. The corresponding rates in mg/min will, of course, depend on the molecular weight of the oil. An average figure deduced from the results of these workers for the 203 pump (unbaffled) operating at the normal heater wattage (250W) is 0·4 mgm/min for DC 702 silicone oil. This figure increased by about 50% on increasing the heater supply to 300W. The graph of back-streaming rate against heater wattage was found to be practically linear over the range from 180 to 300W. The rate of back-streaming was independent of the fine-side pressure at pressures below 10^{-4} torr.

Baffles are provided between the top pump jet and the vacuum tank in order to reduce the amount of back-streaming oil that reaches the tank walls or assembly therein. These baffles are usually water-cooled. The water supply to the pump coils or jacket is first passed through the cooling arrangement on the baffle in the water circuit.

The baffle is arranged so that every back-streaming molecule that is ejected in a straight line collides with it. This 'optical' design may fail, however, to obstruct back-streaming molecules which collide with each other before reaching the baffle (Power and Crawley, PC1). The baffle must, of course, reduce the pump speed: in general, the more restrictive the baffle to back-streaming oil, the more will it reduce this speed.

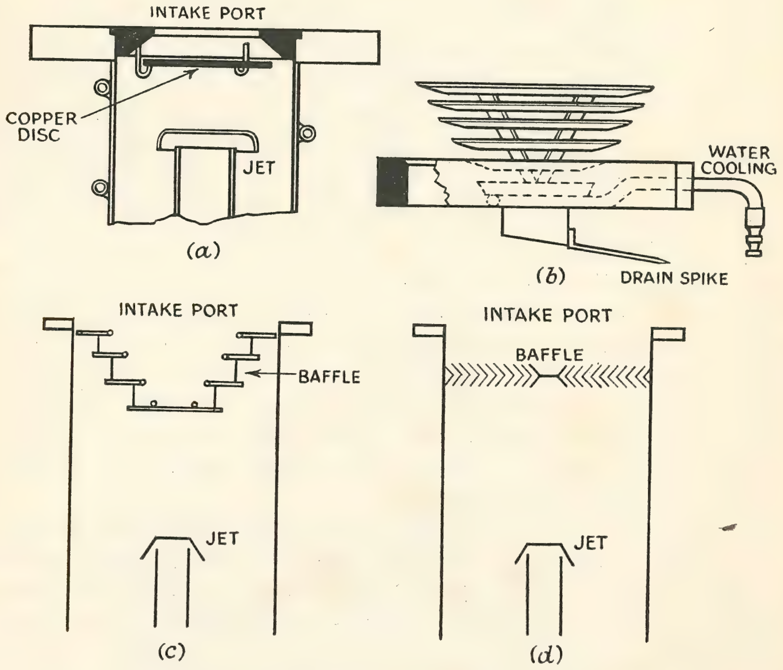


FIG. 2.16 Baffles for oil diffusion pumps

Power and Crawley report that a simple copper disc supported within the pump mouth and cooled only by conduction through the rod support to the pump wall (Fig. 2.16(*a*)) reduces the back-streaming rate by more than 3000 : 1. Other, more complex designs of baffles are illustrated in Fig. 2.16. A drain-away spike is often provided on the baffle and arranged so that the collected oil drips off the baffle back into the pump in a region away from the hot jets and pump chimney.

Fig. 2.14(*b*) illustrates a combined baffle and plate-type isolation valve, as used in the Edwards High Vacuum Ltd. series of oil diffusion pumps. Fig. 2.16(*b*) is an effective type of baffle, model BFL500, used by Gerätebau-Anstalt Balzers for their oil diffusion pumps. Riddiford (R2) describes two types of baffle (Figs. 2.16(*c*) and (*d*)) which he used inside a 16 in. oil-diffusion pump. The stair-case type (Fig. 2.16(*c*)) reduced the pump speed from 2930 litre per sec to 2000 litre per sec, whilst the 'one-hit' model (Fig. 2.16(*d*)) reduced the speed to 1470 litre per sec. Type (*c*) in conjunction with a plate valve (Fig. 2.14(*b*)) was therefore preferred, though it was less effective in preventing back-streaming. Riddiford states that the 'one-hit' right-angle baffle (Fig. 2.16(*d*)) was a 'complete one in preventing the escape of vapour'. He recommends that a baffle of diameter about 50% larger than the pump intake throat diameter should be used for efficient pumps with a good Ho coefficient (§ 2.9). This would, of course, demand a special enlarged baffle-chamber above the pump throat. It is alleged that the advantages of a refrigerated baffle on a large properly-baffled vacuum system are small because the ultimate is decided by real and virtual gas and vapour leaks rather than by the pump. Refrigeration will, however, increase the pumping speed for condensable vapours, provided that, in very large systems, sufficiently large bore tabulation can be used between the refrigerated baffle and the vacuum tank. Alpert (A1) describes a very effective baffle for small glass oil diffusion pumps (§ 8.1). It is in the form of an open roll of corrugated copper foil.

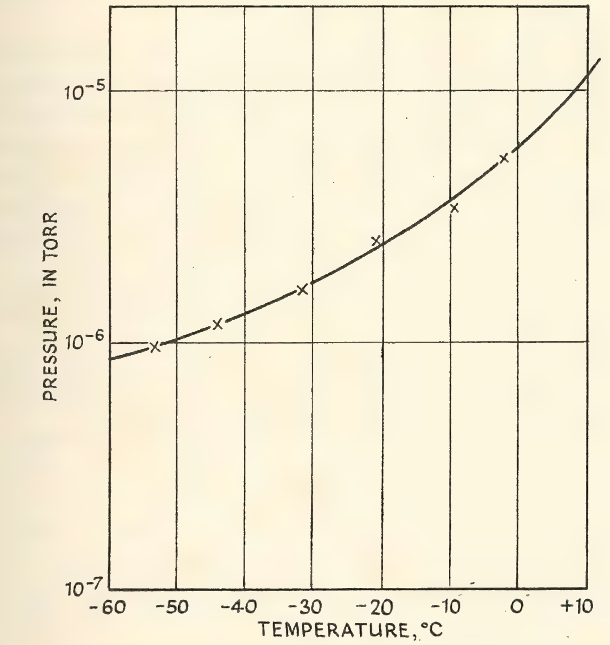


FIG. 2.17 Ultimate pressure against average baffle temperature (*Barton and Turnbull*)

Back-migration is reduced if a baffle is used because the baffle will not be as hot as the pump jets so the vapour pressure of the oil which collects on the baffle will be lower. By cooling the baffle with circulating water—which is usually some 5° C below room temperature—or, preferably, by using a coolant such as brine solution at −10° C, or coolant circulated from a refrigerator, the vapour pressure of the oil, and so the back-migration from the baffle, can be reduced still further. Alternatively, a cold trap (§ 2.11) can be employed. The oil which collects on a refrigerated baffle or trap is lost from the pump; additional pump fluid may have to be added occasionally.

Barton and Turnbull (BT1) give a graph of ultimate pressure against average baffle temperature; an oil diffusion pump with an intake port diameter of 6 in. was used to evacuate a 32 litre vacuum tank in their experiments. Pressure measurements were made with a 'high-speed' ionization gauge (§ 3.9). The equivalent nitrogen pressure—not the true ultimate pressure (§ 2.14)—recorded was $1{\cdot}5 \times 10^{-5}$ torr with the baffle plates at +13° C, which was reduced to $8{\cdot}6 \times 10^{-7}$ torr at a baffle temperature of −60° C after 48 hours pumping (Fig. 2.17).

Another method by which back-streaming into the vacuum tank can be reduced without resorting to refrigeration is to provide a baffle of large effective surface area to which the oil clings firmly in the form of a film a few molecules thick. Such films have significantly lower vapour pressures than the liquid in bulk. The authors have successfully used a baffle of low impedance to gas flow in the form of a thin layer of glass-wool sandwiched between two open wire meshes. An advantage of such a simple, inexpensive baffle is that, after it has become coated with an oil film, say, after a day's use, it can be thrown away and replaced by a fresh sample. Tungsten wool could be used instead of glass wool.

The effect of a plate-valve and baffle of the type illustrated in Fig. 2.14(*b*) on the speed of a diffusion pump is indicated by the figures given in Table 2.1 for the Edwards High Vacuum Ltd. series of oil-diffusion pumps.

TABLE 2.1

Model No.	102	203	403	603	903*B*	1605
Speed,[1] unbaffled (litre/sec)	9–10	70–80	300	600–650	1500	5–6000
Speed, with baffle (litre/sec)	7–8	50–55	170–200	300–350	900	3000

[1] Speed is practically constant over the pressure range from 10^{-3} to 10^{-5} torr.

2.11. Cold Traps

In using mercury-vapour pumps it is essential to instal a cold trap between the pump intake port and the vacuum tank if the total pressure required is to be less than the vapour pressure of mercury at room temperature (10^{-3} torr approx at 15° C (*see* Table A2, p. 517)). This pressure of mercury vapour is only of no account if mercury is not deleterious to the vacuum process undertaken as, for example, in the pumping of mercury vapour rectifiers.

Cold traps of various designs are illustrated in Fig. 2.18 (*see also* Fig. 2.15). The following coolants can be used: ice (0° C); ice-salt mixtures (−10° C approx); solid carbon dioxide mixed with ether, acetone or trichlorethylene (−78° C); liquid air (−187° C) and liquid nitrogen (−196° C). To obtain a total ultimate pressure of 10^{-6} torr, only solid carbon dioxide, liquid-air or liquid nitrogen are satisfactory if a mercury diffusion pump is used, unless mechanical refrigeration is available. At −78° C, the vapour pressure of mercury is calculated, by extrapolation of the vapour-pressure against temperature curve, to be 3×10^{-8} torr, whilst at −187° C it is 3×10^{-31} torr. Though solid carbon dioxide is hence apparently satisfactory because pressures less than 10^{-6} torr are not commonly required, yet liquid air is preferable because water (ice), which is often unavoidably present, has a vapour pressure of 5×10^{-4} torr at −78° C (Table 11.1). Moreover, it is inevitable that the upper parts and inner walls of the trap will be at higher temperatures than the coolant itself.

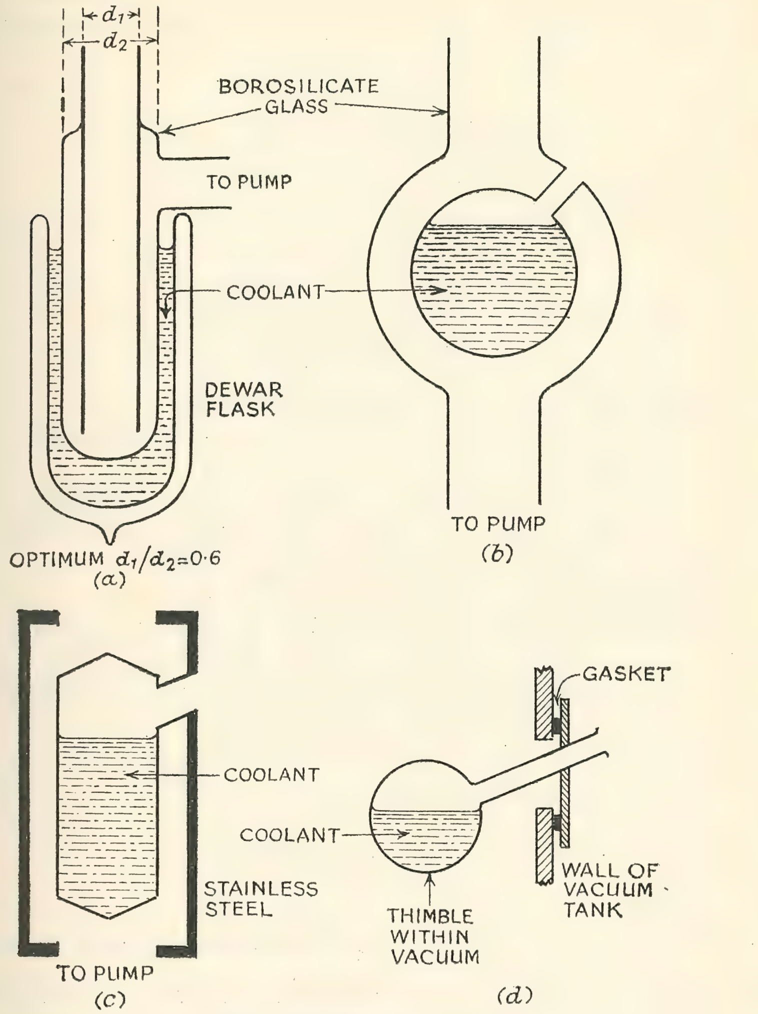


FIG. 2.18 Cold traps

A baffle at room temperature or at an intermediate low temperature should be inserted between the cold trap and the pump to ensure return of the working fluid to the pump. This is particularly necessary in large diffusion pumps, otherwise loss of fluid from the pump might be serious. For example, Power (*see* Yarwood, Y2) reports that a 9 in. oil-diffusion pump (speed 1500 litre/sec without baffle) would lose its oil charge in 5 days.

In using cold traps, particularly if solid carbon dioxide is the coolant, the schedule of operations of the system should be arranged so that the interior of the trap is not exposed to the atmosphere at temperatures below room temperature. Otherwise, water or ice will form in the trap and lead to subsequent vapour pressure difficulties. If such exposure to the atmosphere is unavoidable, it is sometimes worthwhile to warm the trap before re-use to drive off condensed vapours.

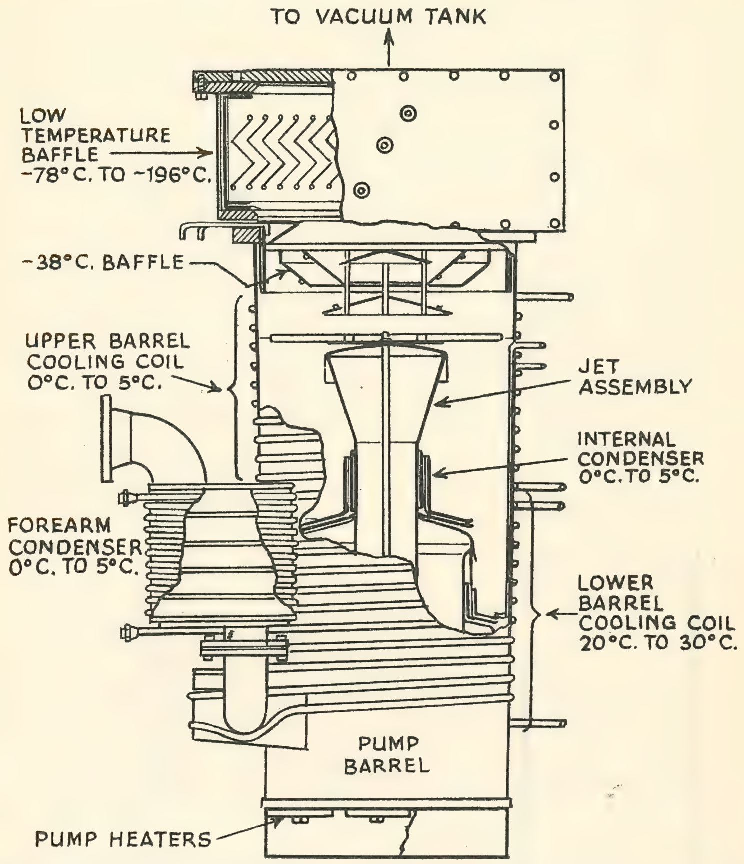

TO VACUUM TANK
LOW TEMPERATURE BAFFLE -78°C. TO -196°C.
-38°C. BAFFLE
UPPER BARREL COOLING COIL 0°C. TO 5°C.
JET ASSEMBLY
INTERNAL CONDENSER 0°C. TO 5°C.
FOREARM CONDENSER 0°C. TO 5°C.
LOWER BARREL COOLING COIL 20°C. TO 30°C.
PUMP BARREL
PUMP HEATERS

FIG. 2.19 A 32-in. diameter mercury diffusion pump (*after H. R. Smith*)

Reimann (R3) reports that, even using a liquid-air trap, it is still essential to proceed with caution if difficulties due to water vapour are to be avoided. Thus, in the pumping of electron tubes, it is necessary to bake the tube in order to degas the glass walls before the liquid-air is applied; otherwise, water vapour released from the heated tube will condense in the regions of the vacuum system near the liquid-air trap which are at temperatures between room temperature and −187° C. If liquid-air is applied during the bake, progressive evaporation of the ice will degrade the vacuum. Reimann recommends using a trap of the type shown in Fig. 2.18(*a*) and immersing the trap to a moderate depth in the Dewar flask during the bake. When the baking is finished, the Dewar flask is raised to immerse the trap completely in liquid-air.

Liquid-air or liquid nitrogen is preferred in all cases except when it is important to prevent the introduction of carbon dioxide gas into the system; for example, in filling Geiger–Müller counter tubes (Le Croissette and Yarwood, LY1). This is because, at liquid-air temperatures, carbon dioxide is frozen out of the atmosphere and may, in subsequent processing, enter the vacuum system because, at −180° C, it has a vapour pressure of $1{\cdot}3 \times 10^{-5}$ torr.

If there is any danger of exposure of the coolant to oil or grease, liquid nitrogen is safe whereas liquid air—which is primarily liquid oxygen—is not. Liquid nitrogen is, however, considerably more expensive and deliveries from the producers are less readily arranged.

Cold traps have the great disadvantage that they inevitably have considerable impedance to gas flow, and so reduce the pumping speed of the system for the permanent gases. It is difficult to design an effective cold trap which does not reduce the speed by at least 40%, and a 60% reduction is not unusual in practical designs. The design of Fig. 2.18(*b*) has been specially developed to provide a high conductance. The use of a cold thimble (Fig. 2.18(*d*)) avoids the reduction of speed but does not prevent satisfactorily the effects of backstreaming. On the other hand, as regards condensable vapours, and even carbon dioxide gas, a cold trap at a sufficiently low temperature has a pump speed of its own. This is because it may be assumed that all the molecules of vapour which impinge on the trap are condensed, provided that the pressure of this vapour at the trap temperature is negligible compared with the total gas pressure in the vacuum tank at room temperature. This is the case for almost all vapours if liquid air or nitrogen is used as the coolant.

If the surface area of the cold trap which is exposed to vapour is A sq cm, then, assuming that molecular flow conditions prevail, and applying equation (1.9) it follows that the pump speed S_t of the trap for a condensable vapour of molecular weight M is given by:

$$S_t = \sqrt{\frac{\mathbf{R}T}{2\pi M}}\, A \text{ cu cm/sec.}$$

Assuming that the average temperature in the vacuum tank is 20° C (293° K), and substituting $\mathbf{R} = 8{\cdot}314 \times 10^7$ erg deg^{-1} mol^{-1},

$$S_t = \sqrt{\frac{3860}{M}}\, A \text{ litre/sec.}$$

It is here assumed that the conductance of the tubulation between the trap and the source of vapour is neglected (a correct assumption if a cold thimble is used).

If water-vapour is concerned, $M = 18$, and

$$S_t = \sqrt{\frac{3860}{18}}\, A = 14{\cdot}6\, A \text{ litre/sec} \tag{2.13}$$

Mechanically refrigerated cold traps are valuable for both large oil and mercury diffusion pumps in that large quantities of liquid-air are avoided. Leever (L2) describes a two-stage refrigerator unit which uses Freon-12 in the first stage and Freon-13 in the second stage operated in tandem. The liquid Freon-13 is conveyed through a capillary line to the baffle-trap where it evaporates and is then returned to the compressor unit in a closed, hermetically sealed circuit. A baffle temperature of −93° C can be maintained.

In an elaborate arrangement to prevent mercury from entering the vacuum tank when a 32 in. mercury diffusion pump is used (Fig. 2.19), (Smith, S3), an optically opaque baffle at −38° C (provided by a mechanical refrigerator) is arranged directly above the top jet of the pump, and above this is a second, low temperature baffle maintained at −78° C (solid carbon dioxide) to −196° C (liquid nitrogen). Smith suggests that −78° C is the maximum permissible temperature; he also mentions a prototype mechanical refrigeration unit able to provide temperatures of −130° C. Kennedy and Smith (KS1) describe a two-stage mechanical refrigeration system for temperatures of −90° C which can be used to cool the upper baffle.

2.12. Deleterious Effects of Back-streaming and Back-migration

The collection of thin—even monomolecular—films of oil on structures in a vessel undergoing evacuation by an oil diffusion pump may introduce difficulties. Refined hydrocarbon oils like the Apiezon oils (Table 2.2) may well introduce carbonaceous deposits on electrodes which have been heated or bombarded with electrons or ions, and these deposits may be electrically conducting or non-conducting depending on their formation, whilst semi-organic polymers, such as the silicone oils (Table 2.2) introduce insulating deposits which are probably a sub-oxide of silicon, and can only be removed by subsequent heating to 450° C.

Such thin film deposits are of no account in many vacuum operations. In some cases, however, the presence of such deposits will spoil the required characteristics. Examples are found in operational conditions in mass spectrometers, ion accelerators, electron tubes with oxide-coated cathodes (Herrman and Krieg, HK1), photoelectric cells, the preparation and study of secondary-emitting surfaces (Lempicki and McFarlane, LM1), the vacuum deposition of rhodium, and apparatus where high-voltage insulators must retain clean surfaces (Power and Crawley, PC1).

The general opinion seems to be that silicone oils cause more trouble in this connection than the truly organic materials, and that the organic esters (Table 2.2) are preferred if most freedom from contamination is required. In mass-production schedules for electron-tube manufacture, the vessel is kept hot relative to the pumps throughout the processing and the activation of thermionic cathodes is performed after the seal-off from the pumps. The possibility of back-streaming deposits being harmful is then very remote. On the other hand, in experimental work with demountable tubes, heating and the use of getters (§ 6.8) is impracticable, and the effect of deposits arising from back-streaming and back-migration may be so harmful as to render

impossible the use of an oil diffusion pump without a cold trap. In general, especially for small-scale plant, it is therefore best to use a mercury diffusion pump and liquid air trap, or an oil diffusion pump with a liquid nitrogen trap.

Latham *et al.* (LPD1) report that Ellis has investigated the sources of contamination formed on surfaces in an evacuated vessel above a diffusion pump when such surfaces are subject to electron bombardment, and concludes 'that the back-streaming oil from the diffusion pump is not by any means the sole or even the most important factor. Fore-pump oil migrating into the system during rough-pumping, gaskets, finger-prints and dirt generally make such important contributions that, even if liquid nitrogen traps are used above the oil diffusion pumps, or if mercury pumps are used, there may be little or no reduction in the contamination rate'.

It may well be proved in the future that the ion pump (§ 7.1), in conjunction with a fractionating or self-purifying oil diffusion pump, will provide an alternative to the use of a liquid-air trap. However, the value of liquid-air in covering up some of the sins of omission in the design or operation of an experimental system is very great!

TABLE 2.2

Fluids for use in vapour stream pumps

Fluid	Chemical Nature	Formula	Molecular Weight	Specific Gravity at 25° C	Vapour Pressure at 25° C torr	Boiling Point at 10^{-2} torr °C
Amoil[1]	i-diamyl sebacate	$C_8H_4(COOC_5H_{11})_2$	306·2	1·0190	10^{-5}	
Amoil S[1]	,, ,,	$C_8H_{16}(COOC_5H_{11})_2$	343·3	0·9251	10^{-6}	111
Apiezon A[3]	hydrocarbons		mean 414[5]	0·8735 at 15° C	2×10^{5}	
,, B[3]	,,		,, 468[5]	0·871 at 15° C	4×10^{-7}	110
,, C[3]	,,		,, 574[5]		10^{-8}	125
,, G[3]	,,				10^{-6}	
,, BW[3]	,,				10^{-7}	
Butyl phthalate[1]	*n*-dibutyl phthalate	$C_6H_4(COOC_4H_9)_2$	278·1	1·0465	3×10^{-5}	85
Butyl sebacate[1]	*n*-dibutyl sebacate	$C_8H_{16}(COOC_4H_9)_2$	314·3	0·933		90
Myvane 20				0·853		
Narcoil 10[4]	chlorinated diphenyl		326	1·54	3×10^{-4}	
Narcoil 20[4]	Same as Octoil S					
Narcoil 40[4]	Same as Octoil					
Octoil[1]	*d*-2-ethyl hexyl phthalate	$C_6H_4(COOC_8H_{17})_2$	390·3	0·9796	3×10^{-7}	122·5
Octoil S[1]	di-2-ethyl hexyl sebacate	$C_8H_{16}(COOC_8H_{17})_2$	426·3	0·9103	3×10^{-8}	143·5
Silicone DC702[2]	Methyl polysiloxanes		530	1·07	10^{-6}	160
Silicone DC703[2]	Methyl polysiloxanes		570	1·09	10^{-7}	200
Plasticizer	tri-*m*-cresyl phosphate		368			
,,	tri-xylenyl phosphate	$((CH_3)_2C_6H_4)_3PO_4$	414			
,,	glycerol	$(CH_2OH)_2CH(OH)$	92		5×10^{-5} at 15° C	

[1] Data by courtesy of Consolidated Electrodynamics Corporation.

[2] Courtesy of Dow Corning Corporation.

[3] Courtesy of Shell Chemical Co. Ltd. Apiezon A is similar to Leybold oil D; Apiezon B is similar to Leybold oil E.

[4] Courtesy of National Research Corporation. In Britain, Narcoil is known as Viacoil, and is obtainable from Vacuum Industrial Applications Ltd.

[5] Experimental determination of Burrows and Jackson (BJ1).

2.13. Fluids for Use in Vapour Stream Pumps

Apart from mercury,* Table 2.2 gives data on several of the fluids which have been used in vapour pumps. Table 2.3 indicates the properties such fluids should possess and the extent to which they are satisfied. There is not a liquid available which has all these properties, or even most of them. Therefore, the selection of a suitable fluid for use in a vapour pump is a matter of compromise. Fortunately, oils are available which satisfy fairly well the more important of the requirements specified. These oils are broadly classifiable as refined hydrocarbon oils (Burch, B1), certain esters of phthalic and sebacic acids (Hickman and Sanford, HS1) the Arochlors (chlorinated biphenyls) and the semi-organic silicones (Brown, B2).

TABLE 2.3
Requirements of fluids for use in vapour pumps

Quality required	Remarks
Low vapour pressure	Range from 10^{-5} torr to 10^{-8} torr available (*see* Table 2.2.).
Resistance to oxidation when heated at, or near, atmospheric pressure	Silicones 702, 703 and 704 and also Narcoils withstand such oxidation well, but other fluids listed in Table 2.2 oxidize to give tarry and solid deposits (§ 2.15).
Freedom from volatile constituents	Distinct chemical substances such as tri-xenyl phosphate and other plasticizers, also octoils, are best. Remedy to avoid effects of volatiles is to use a fractionating or self-purifying pump (§ 2.14).
High molecular weight to facilitate effective pumping	Except for glycerol, molecular weights are all above 300.
Resistance to decomposition on heating *in vacuo*	Decomposition of fluid into permanent and semi-permanent gases limits ultimate vacuum obtainable (§ 2.14). Silicone DC702 least prone to this difficulty.
Resistance to catalytic decomposition on exposure, when hot, to metal surfaces of pump	Copper used for fabricating pump jets and chimney is unsuitable in this respect as it gives rise to greater catalytic action than other metals with good thermal conductivity, *e.g.* aluminium. Brass, iron, zinc and tin are attacked by oil, but chromium, lead and nickel are not. Galvanizing and soft-soldering should therefore be avoided in pump jackets and jet systems. Chromium or nickel plating of parts is useful.
Resistance to decomposition on exposure to hot filaments or in a gaseous discharge	All fluids used are prone to decomposition in both cases. Not a serious drawback, but means that readings of ionization gauges of both hot-cathode and cold-cathode types are subject to large errors.
Non-hygroscopic	Of fluids shown in previous table, only glycerol is fairly hygroscopic.
Low ability to dissolve gases and vapours	All oils dissolve gases and vapours to some extent. This affects ultimate pressure obtainable because of back diffusion (§ 2.14).
Chemical inertness	Fluids used are reasonably inert to most of materials commonly encountered in vacuum practice. They react, however, with halogens, acid vapours, alkali and alkali-earth metals.
Resistance to decomposition to solid deposits on metal electrodes, etc. (§ 2.12)	None of fluids used is completely free from this defect. Amoils and octoils probably best.
Suitable viscosity–temperature characteristics	Obtainable with all fluids listed. Viscosity of DC702: 290 centistokes at 0° C 28 „ „ 25° C 3·5 „ „ 100° C DC703: 470 „ „ 0° C 58 „ „ 25° C 6·5 „ „ 100° C

---

* Glycerol has also been used (Alexander, A2), but its hygroscopic nature has tended to debar subsequent developments.

Huntress, Smith, Power and Dennis (HSPD1) have recently described a new silicone pump fluid, DC 704, which has high stability and low vapour pressure. It is a single component material which is not only markedly resistant to damage by heating in air but also resists damage from nuclear radiations. It has a molecular weight of 484, a boiling point of 410° C at 760 torr and 189° C at 10^{-1} torr and enables a high boiler pressure to be maintained, so permitting a high forepressure tolerance and high mass throughput. DC 704 is now available in commercial quantities in Britain and America.

Jaekel (J2) reports that these pump fluids suffer some photochemical decomposition on exposure to light and recommends that they be stored in opaque bottles.

Fumes from some hot oils are irritating to the eyes and skin.

The pump body and jet system should be clean and dry and the correct charge of oil (as given by the pump manufacturer) poured into the pump body before the jet assembly is inserted.

2.14. Ultimate Pressures Provided by Oil Diffusion Pumps

The factors which contribute to the residual pressure obtained in a vacuum tank after pumping with an oil diffusion pump backed by a rotary pump may be listed as follows (Latham, Power and Dennis, LPD2; Florescu, F1; Haefer and Winkler, HW1; Reich, R4):

(*a*) Leakage of air into the vacuum tank.

(*b*) Outgassing of the inner walls of the vacuum tank.

(*c*) Outgassing of the sealing material used, *e.g.* rubber or Neoprene.

(*d*) Gases or vapours which have returned from the fore side of the pump by back-diffusion through the vapour jets; added to this, there will be gas or vapour which has gone into solution at the forepressure in the condensed pumping fluid, returned to the boiler, and subsequently liberated through the jets.

(*e*) Gases and light vapours produced by continuous decomposition in the boiler of some of the pumping fluid, and afterwards liberated through the jets.

(*f*) Vapour of the pumping fluid itself or of its constituents.

Of these factors, the first is a matter of design of the vacuum tank, selection of the construction materials used, choice of satisfactory methods of making seals, unions and joints (*e.g.* correct use of O-rings, § 4.17) and the adoption of a sensitive leak-finding technique (Chapter 9).

In the following discussion of ultimate pressures attainable, it is assumed that the vacuum system is air-tight, or rather that the speed at which air can leak into the apparatus is insignificant compared with the speed of the pump.

Outgassing of the inner walls of the vacuum tank and sealing materials (factors *b* and *c*) is often overlooked. Indeed, Haefer and Winkler (HW1) put forward evidence to show that many of the published results on the factors deciding the ultimate have disregarded the important effects of surface films on the inner walls of the system and of the outgassing of, for example, Neoprene O-rings. The curves of Fig. 2.20 (HW1) show (1) the effect of vapours from Neoprene O-rings used as seals in the system, (2) the improvement resulting from a preliminary degassing of these O-rings on heating them in a separate vacuum vessel for 2 hours at 90° C before using them in the system, (3) the improvement obtained if aluminium O-rings are employed instead of Neoprene rings.

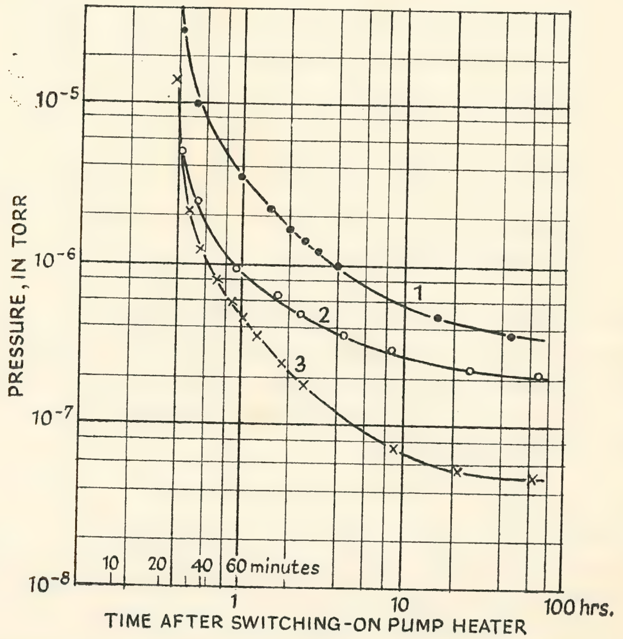


FIG. 2.20 Pressure–time curves obtained using various O-ring seals: (1) Neoprene, fresh, non-degassed: (2) Neoprene, degassed for 2 hours at 90° C in a separate vacuum system: (3) aluminium. A three-stage G.A.B. oil diffusion pump, Diff 120 (with baffle, speed 90 litre/sec) filled with Apiezon C oil was used. Pressure measured with a thermal ionization gauge calibrated for air (§ 3.9)

The factor (*d*) can be reduced to an insignificantly low level because back-diffusion is very small in a multi-stage pump with dense ejector jets for the second and third stages.

The factors (*e*) and (*f*) are those of most importance in limiting the ultimate obtainable provided that the vacuum tank is leak-free, does not outgas significantly, and if sealing materials with a low outgassing rate are used (*e.g.* aluminium O-rings in a metal system, *see* § 4.27).

According to Reich (R4) the vapour pressure of the pumping fluid is the more important of the two factors (*e*) and (*f*) if the baffle temperature exceeds 20° C. If the pumping fluid is a true chemical compound (*e.g.* Narcoil 40, Octoil, dibutyl phthalate) then the vapour pressure is a certain value at a given temperature. If, however, the pumping fluid is a mixture of chemical

compounds (*e.g.* Apiezon oils, silicone DC 703), then the vapour pressure of interest is that of the most volatile component. At baffle (or cold trap) temperatures below about 20° C the decomposition products of the pumping fluid (factor *e*) are the most important contribution to the ultimate vacuum. As the decomposition products certainly contain non-condensable permanent gases, even a liquid-nitrogen filled cold trap is incapable of reducing the ultimate due to them. In this connection, mercury, which cannot decompose, is, if it is thoroughly cleaned, superior to oil.

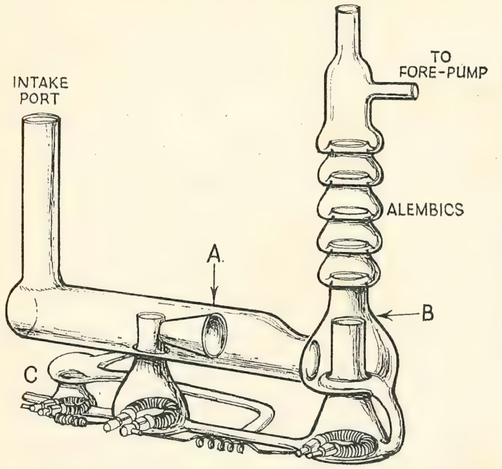
The effect on the ultimate pressure of the vapour pressure of the pumping fluid (and of its constituents) is considerably reduced by using either a **fractionating pump** (Hickman, H2) or a **self-purifying pump** (LPD2). The design of an all-glass fractionating pump is shown in Fig. 2.21; its operation is explained in the accompanying legend. The Edwards High Vacuum Ltd. self-purifying pump (Speedivac F203), which is a development from the normal model, 203, is illustrated and explained in Fig. 2.22.

The rate of thermal decomposition of the pumping fluid is accelerated by increasing the boiler temperature and by the catalytic action of the metal of the pump. For this latter reason, a glass pump is preferable to a metal one as regards the attainment of a low ultimate pressure (Jaeckel, J2). Decomposition of the fluid is decreased by the use of a lower forepressure because boiling of the fluid will occur at a lower temperature.

Autocatalytic decomposition is discussed by Latham *et al.* (LPD2) where breakdown of the pumping fluid is accelerated by the accumulation of decomposition products. As these products are largely ejected from a self-purifying pump, such autocatalytic effects are minimized. Curves published by Latham *et al.* of ultimate pressure against time show that the self-purifying pump F 203 always conditions more rapidly to a lower pressure than a standard 203 pump. Moreover, such conditioning times, using the F 203, are as short if commercial plasticizers such as tri-cresyl phosphate (Table 2.2) are used, as are obtained with specially prepared pumping fluids such as Apiezon C and DC 702, but this is not so where a pump without self-purifying means is employed.

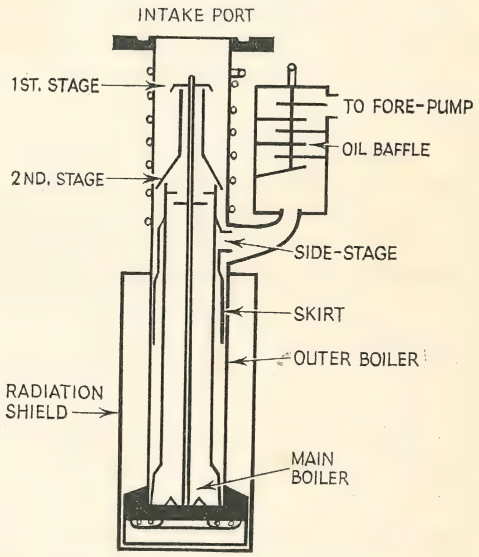
Haefer and Winkler (HW1) describe typical G.A.B. metal oil diffusion pumps in which purification of the pumping fluid is achieved. The cooling jacket around the pump body is only extended downwards as far as is necessary to ensure adequate working of the lowest jet of a three-stage pump. The pump casing is therefore heated in the region of the forevacuum to such an extent that the condensed pumping fluid which flows backwards down the walls is freed from its thermal decomposition products before it returns to the boiler. The top jet—first stage—operates only with the fractionated components of the pumping fluid which have the lowest vapour pressure. The bottom of the pump casing—the boiler region—has corrugated walls to avoid overheating of the oil; the heat transfer from the heater to the oil thus takes place through a large surface area.

The recording of the ultimate pressures attainable by diffusion pumps is usually done with a 'high-speed' thermal ionization gauge (§ 3.9). This is



Oil has components of various vapour pressures. The most volatile constituents are distilled into the alembics; those of medium volality form the vapour streams at the second-stage jet B and the first-stage jet A. The boiler C acts as a still in which tarry residues collect. Using Octoil S as the pumping fluid, an intake pressure of 5×10^{-7} torr is provided with a max. forepressure of 0·2 torr

FIG. 2.21 A glass fractionating pump



The oil returning from the first- and second-stage jets passes a skirt and falls as a thin film down an elongated pump wall to the boiler. As this part of the pump is surrounded by a radiation shield, it forms an outer boiler which supplies vapour to the side-stage only. Hence lighter fractions of the oil vaporize first as the oil returns by this path, so the fluid which finally enters the main boiler is partly freed of the more volatile constituents. As the first stages are fed from the main boiler, the vapour pressure of the fluid there is reduced

FIG. 2.22 A self-purifying pump

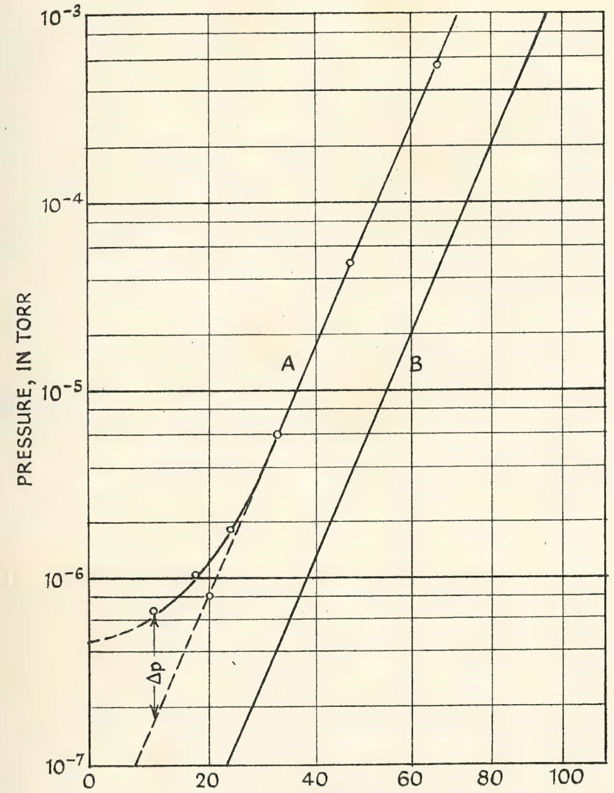


FIG. 2.23 Comparison of the ultimate pressure against temperature curve with the vapour pressure against temperature curve for Octoil (*after Reich*)

preferably of the Bayard–Alpert pattern (§ 3.9), so that the residual X-ray effect is minimized and pressures down to 10^{-9} torr or lower can be recorded. These gauges are usually calibrated for air. The pressure readings taken are hence equivalent air pressures. The true pressures prevailing at the ultimate of an oil-diffusion pump are consequently not known with certainty because (*a*) the specific ionization obtained when electrons pass through oil vapour is considerably greater than when they pass through air at low pressure, (*b*) the oil decomposes both in the pump and at the hot filament of the gauge. It is, however, certain that the readings of ultimate pressures so recorded are too high. Jaeckel (J1) gives an example of an ultimate recorded by an ionization gauge as $1{\cdot}2 \times 10^{-5}$ torr, whereas a molvakuummeter (§ 3.5) gave a reading of 2×10^{-6} torr. This second reading is the more accurate, but neither instrument is really capable of recording low gas pressures independently of the nature of the gas molecule. The ratio of pressures recorded by Jaeckel was 6 : 1. Haefer and Winkler (HW1) give a ratio of recorded to true pressure of 12 : 1. Reich (R4) compared the curve A of the ultimate pressure-against-temperature (of the thoroughly degassed measuring chamber and baffle) with the vapour pressure-against-temperature curve B of the oil (Fig. 2.23). The ultimate was recorded by an ionization gauge whereas the vapour pressure-temperature curve of the fluid was determined absolutely in a separate experiment. For pumping fluids which are true chemical compounds the two curves are exactly parallel to one another at the higher temperatures. The pressure difference Δp between the prolongation to low temperatures of the straight part of the ultimate pressure-temperature curve and the measured values is a constant independent of the temperature. These results indicate that the ultimate is decided by the vapour pressure of the pumping fluid at the higher temperatures (above 28° C for Octoil) whereas at the lower temperatures it is decided by the non-condensable decomposition products of the fluid. The sensitivity of the ionization gauge for the pump fluid relative to that for air can be deduced from the amount by which the straight part of the ultimate pressure-temperature curve exceeds the vapour pressure-temperature curve. For an ionization gauge with a sensitivity of $S\mu A/mA/micron$ for air, the sensitivities were deduced in this way to be 13S for Narcoil 40, 13S for Octoil and 9·2S for dibutyl phthalate.

What are the ultimate pressures obtainable by oil diffusion pumps? If a three-stage glass fractionating diffusion pump with Octoil S, Apiezon C or DC 703 is used to evacuate a glass vessel which has been degassed for about one hour at 400° C, the ultimate total pressure recorded by a thermal ionization gauge is about 5×10^{-8} torr. This probably corresponds to an actual total pressure of 10^{-8} torr, or even somewhat less. As regards the use of metal pumps and vacuum tanks, the self-purifying pump with a baffle to limit back-streaming is good practice. However, there are considerable disparities between the published results of the ultimates recorded by a thermal ionization gauge when such practice is adopted. Figures given by Latham *et al.* (LPD2) are summarised in Table 2.4.

TABLE 2.4

Fluid	Early model of Edwards 203 pump without self-purifying means		Edwards F203 (self-purifying means)	
	Pressure in torr at		Pressure in torr at	
	Room temp.	−40° C approx.	Room temp.	−40° C
Silicone DC 702	$2·3 \times 10^{-5}$	$3·2 \times 10^{-6}$	$4·2 \times 10^{-6}$	$2·3 \times 10^{-7}$
Silicone DC 703	$4·2 \times 10^{-6}$	$1·6 \times 10^{-6}$	$5·2 \times 10^{-7}$	5×10^{-8}
Apiezon C	$5·2 \times 10^{-6}$	$1·4 \times 10^{-6}$	$3·2 \times 10^{-7}$	$1·3 \times 10^{-7}$
Tri-cresyl phosphate	$7·4 \times 10^{-6}$	$5·3 \times 10^{-6}$	$7·8 \times 10^{-7}$	$8·8 \times 10^{-8}$

The ultimate pressures recorded after cooling (solid carbon dioxide was used around the pump header containing the gauge) are alleged to be largely due to the pressure resulting from decomposition of the oil into gases.

These figures are suspect because the pump header was only degassed by heating before assembly of the system, and Neoprene O-rings were used. Even at −40° C (and the central region of the header is not cooled to the same extent as the outer walls where the solid carbon dioxide is placed) the vapour pressure of ice (aqueous films may well be trapped on non-degassed metal walls) is 10^{-1} torr. However, these results are valuable as it is not usual practice to degas metal vacuum tanks by heating after they are assembled on the pumps.

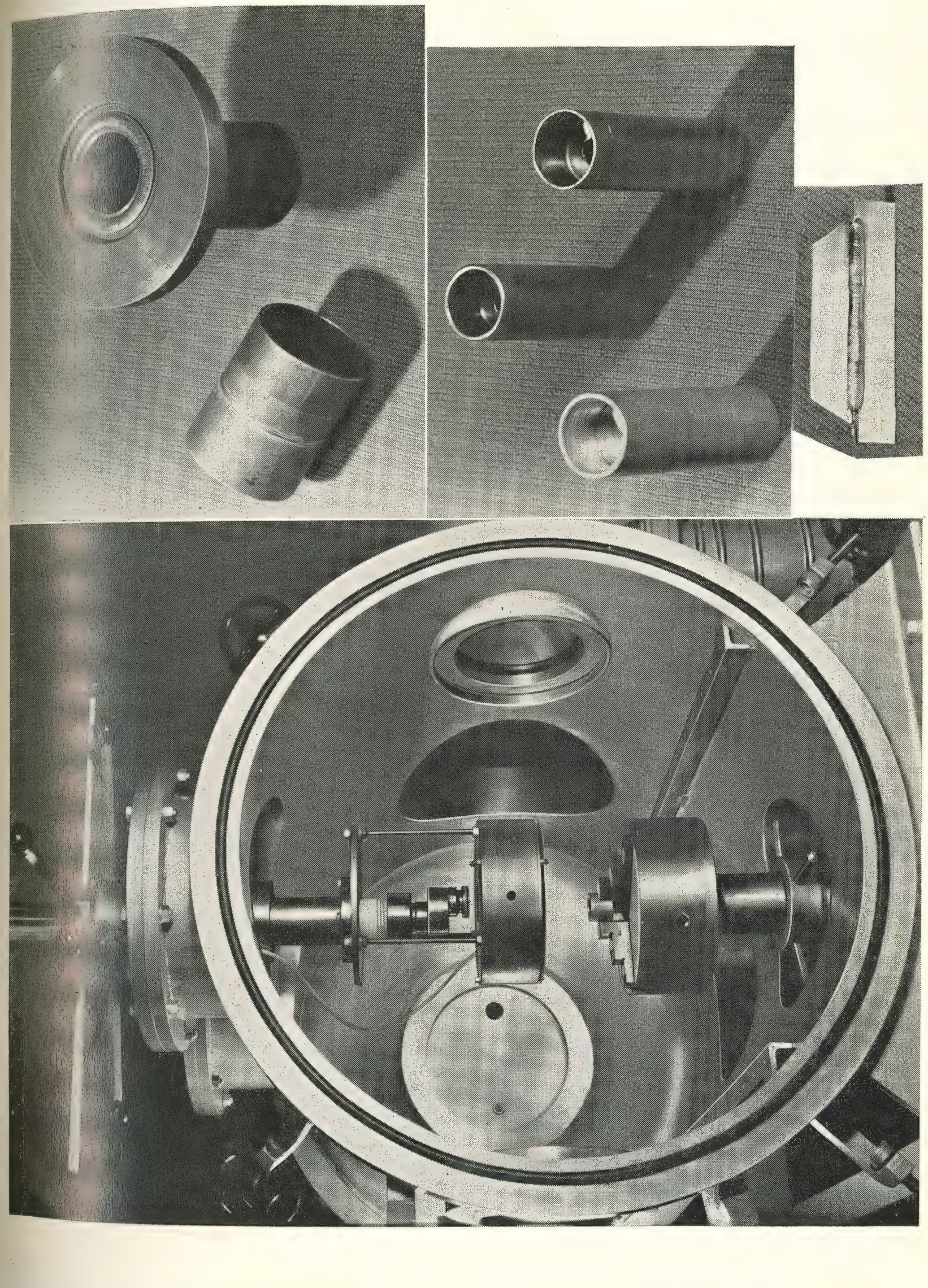
Haefer and Winkler (HW1) publish curves (Fig. 2.24) of the ultimate pressures obtained with a G.A.B. Diff 120 self-purifying oil diffusion pump using

Plate 4

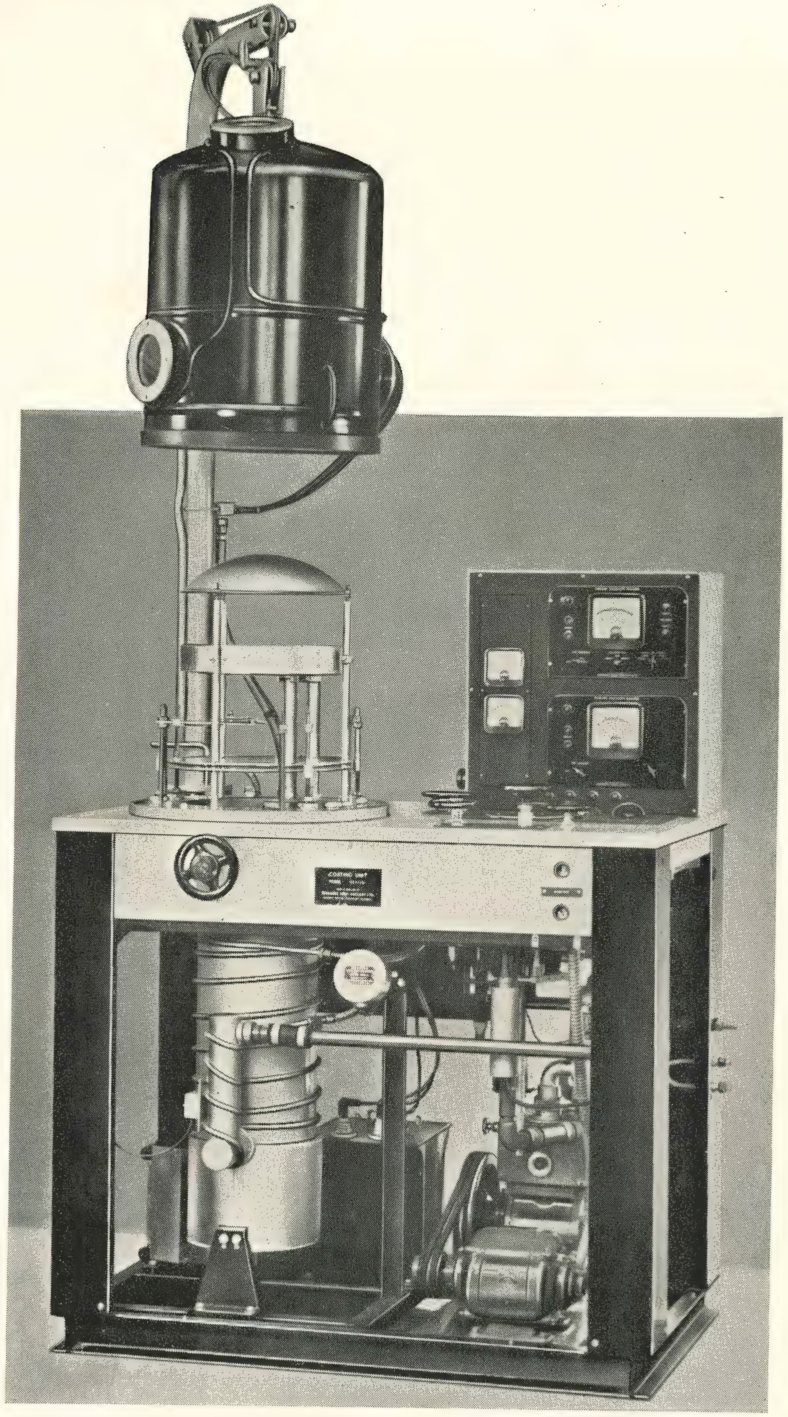
Electron beam welding

Left: Close-up view of interior of vacuum chamber showing work in chuck.

Right: (*top*) butt-weld between mild steel tubes, also flange to pipe adaptor edge-welded in $\frac{1}{4}$ in. copper; (*centre*) edge-welding on end caps, tube on left-hand side is aluminium, in middle, nickel, and on right-hand side, stainless steel; (*bottom*) welded 0·01 in. molybdenum sheet (*see* p. 151).



Courtesy of Edwards High Vacuum Ltd.



Courtesy of Edwards High Vacuum Ltd.

Plate 6

Commercial plant for vacuum coating, Model 18E4 (*see* p. 386).

Apiezon C oil. In this case the pump header was degassed by heating at 100° C for some hours. The ultimate pressure obtained with the pump head and baffle at $-40°$ C is slightly less than 4×10^{-8} torr if aluminium O-rings are used as seals (curve 3). This is three times lower pressure than that recorded at $-40°$ C by Latham *et al.* (Table 2.4) using Apiezon C oil but where the pump header was only degassed before assembly of the system and Neoprene O-ring seals were used.

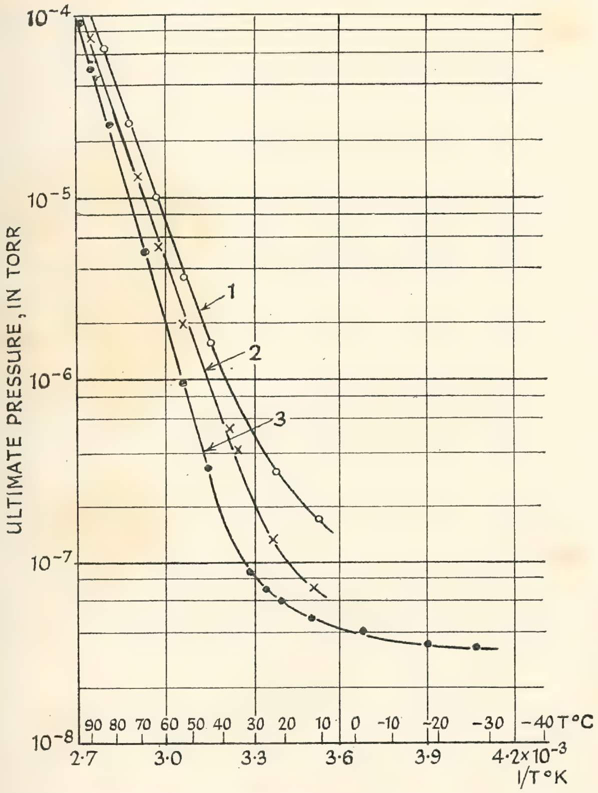


FIG. 2.24 Ultimate pressure as a function of the temperature of the pump header and baffle for various sealing ring materials: (1) Neoprene, degassed for 5 hours at 90° C: (2) Neoprene, degassed for 18 hours at 90° C: (3) aluminium

Latham *et al.* allege that the ultimate pressure is largely decided by the gaseous decomposition products of the oil if a refrigerated baffle (at, say, $-10°$ C) is used. Reich (R4) implies that this is true even for baffles cooled only by tapwater (at somewhat less than 20° C), though this conclusion should probably be accepted with some reserve. These results indicate that it is preferable to use a pumping fluid with a lower boiling point at the fore-pressure to minimize gaseous decomposition products. Hence DC 702 will give a lower ultimate than DC 703 if a refrigerated baffle is used, despite the fact that it has the higher vapour pressure, because it boils at a lower temperature and is more stable. Again, Apiezon A boils with less decomposition than Apiezon B, which has the lower vapour pressure. Hickman is reported by Reimann (R3) as asserting that butyl phthalate evolves less gas under operating conditions in a pump than does hexyl phthalate, the vapour pressure of which at 20° C is less by a factor of 100.

The use of a refrigerated baffle therefore gives the following advantages: less back-streaming and back-migration; a lower ultimate pressure; the use of a cheaper oil of greater thermal stability and lower boiling point.

If the electric power supplied to the heater of a vapour pump boiler is varied, the ultimate fine-side pressure will change. Below a fairly distinct threshold value of heat input, the pump will not operate because the vapour from the jets becomes insufficiently dense to prevent back-diffusion. According to Guthrie and Wakerling (GW1) this threshold value is approximately equal to the power which is lost by radiation from the pump nozzles and chimney—considering these as black-body radiators—at the temperature of the boiling pump fluid. If the heater input wattage is reduced by some 20% below the normal rating, the ultimate fine-side pressure is reduced because of reduction of thermal decomposition products of the fluid with temperature; speed is, however, sacrificed. If the heater input is raised noticeably above the normal, the ultimate fine-side pressure rises because of enhanced thermal decomposition.

The variation of the forepressure from about 0·1 to 10 times the normal value recommended does not affect seriously the fine-side pressure of a two- or three-stage vapour pump. At higher forepressures than 10 times normal, the fine-side pressure and the pumping speed deteriorate rapidly.

Inordinate reduction of heater input or increase of forepressure leads to weakening of the vapour stream from the jets, especially near the cooled walls of the pump casing. Air from the forepressure side will then escape up the inside wall to the fine-side against the reduced action of the vapour stream which is endeavouring to compress the gas.

2.15. Resistance of Pump Fluids to Oxidation

If an almost completely inert fluid is required as regards non-oxidation on exposure to the atmosphere when hot, mercury is the best choice. Oils differ in this respect markedly, but there is little doubt that the silicones are the most oxidation-resistant. In an exhaustive series of tests, Latham, Power and Dennis (LPD1) subjected a number of pump fluids to the drastic treatment of using them in an Edwards 203 oil diffusion pump and then repeatedly admitting air at atmospheric pressure whilst the pump heater was left on. Photographs of the pump interior assemblies published in their paper show clearly that, of the fluids tested, only Silicone 702 and 703 and chlorinated diphenyls (Narcoils) withstand this ordeal satisfactorily. The other fluids used (esters and hydrocarbons) all ultimately gave rise to tarry and solid carbonaceous deposits on the jet system which severely restricted the operation of the pump.

In the mass production of cathode-ray rubes, diffusion pumps with silicone oil (or Narcoil) are frequently used so that any ingress of air to the hot pump does not cause oxidation of the pump fluid. Smith and Saylor (SS1) describe briefly an assembly for the aluminizing of television cathode-ray tube screens in which the evacuation is undertaken with diffusion pumps using silicone oil. Two valves only were used: one between the fore-pump and the diffusion pumps, the other for admitting air. The preliminary evacuation of the tube by the fore-pump is done through the hot diffusion pump, yet no oxidation of the silicone oil occurs. In such cases, however, a baffle or condenser must be provided between the diffusion and fore-pumps, otherwise there will be excessive carry-over of the pump fluid into the fore-pump. Edwards High Vacuum Ltd. provide a 'fluid economiser' for use on valveless pumping systems. This is a baffle inserted in the discharge outlet of the oil-diffusion pump to the fore-pump. The baffle comprises a series of plates which impose abrupt changes of flow direction on the discharged gas, and so on the 'mist' of pump fluid discharged towards the fore-pump. About 70% of the oil vapour discharged is thereby recovered.

Despite the non-oxidization of silicone oils, it is considered better practice to use automatically controlled magnetic isolation valves in mass production cycles to avoid as far as possible the admittance of air to the heated diffusion pump.

2.16. Oil *vs* Mercury

Some data has already been included to enable a choice to be made between a low vapour pressure oil and mercury as a fluid for a vapour pump. This data and other noteworthy points may be summarized as follows:

Mercury

Advantages	Disadvantages
An element—cannot decompose Does not oxidize when heated at atmospheric pressure unless heating is violent and prolonged Does not react with or dissolve commonly encountered gas and vapours Easily purified by distillation High density facilitates return to high pressure boiler High fore-pressures—up to 40 torr—can be used in multi-stage pump	High vapour pressure: $1{\cdot}38 \times 10^{-3}$ torr at 20° C Liquid air trap of inevitably low conducttance is essential if low total pressure is to be attained Amalgamates with many metals; restricts choice of pump construction material; steel and glass is used for pump jackets and jet systems Sensitive as a pump fluid to small traces of oil or grease

Oils

Advantages	Disadvantages
Low vapour pressures obtainable: 10^{-8} torr possible Cold trap unnecessary in many vacuum processes High conductance baffle which prevents most of back-streaming is readily used	Complex compounds or mixtures of compounds: decompose slightly on heating *in vacuo* in boiler Except for silicones and Narcoil, readily oxidized on heating in air Dissolve all kinds of gases and vapours to form solutions and metastable compounds. Decomposition accelerated by catalytic action of some metals, especially copper

Oils *continued*

Advantages	Disadvantages
Inert to metals chosen for pump construction (except that some metals, *e.g.* copper, instigate catalytic decomposition of heated oil). Aluminium or nickel-plated copper usual	Decompose on hot filaments, and in electric discharge. Gases, vapours and some solid deposits formed. (Reports that silicone oils are inclined to affect adversely the sensitivity of ionization gauges due to the formation of insulating deposit on collector plates are alleged to be incorrect for recently developed silicones, Smith and Saylor, SS1)
Self-fractionating or self-purifying pumps can be built to exclude lighter, more volatile fractions of pump fluid	Boiler pressures less than 0·5 torr are necessary in a diffusion pump (assuming no second and third ejector stages) otherwise oil decomposition is accelerated at high boiler pressures and temperatures
	Not readily refined by distillation before use

The ability to use a high forepressure with a mercury vapour pump has led to the somewhat unusual systems in which such a pump is used to 'back' an oil diffusion pump. For example, to evacuate the Philips electron microscope, a small mercury-vapour pump is thus employed. The forepressure to the two pumps in series can then rise to 4 torr without affecting the fine-side pressure in the electron microscope. Consequently, the mechanical rotary pump can be switched off for long periods and an evacuated reservoir used as a 'backing' space to the mercury vapour pump.

2.17. Characteristic Curves of Diffusion Pumps

Like the mechanical rotary pump (§ 2.1) the characteristics of diffusion pumps are generally plotted in the form of speed (in litre per sec, usually) against the fine-side pressure. Alternatively throughput, or mass throughput, against pressure may be plotted. For reasons discussed below this latter procedure is often preferable.

The volumetric speed is essentially constant for unbaffled diffusion pumps over the range of pressures from the ultimate up to between 10^{-3} and 5×10^{-3} torr. The ultimate pressure, as considered in § 2.14, depends on a number of factors, but it is in the region of 5×10^{-6} torr for non-self purifying and non-fractionating pumps under average working conditions without a refrigerated baffle. At the ultimate, and below this pressure, the speed is, of course, zero. The characteristic therefore exhibits a sharp drop from the rated speed to zero at the ultimate, but it is not easy to obtain this region of the characteristic in a practical experiment because the ultimate pressure is not always well defined in terms of the reading of the vacuum gauge. The high-pressure region of the characteristic exhibits a comparatively gradual change of volumetric speed with pressure: usually, the speed begins to fall at about 10^{-3} torr, but may still be a significant fraction of its rated value at 10^{-1} torr. These figures and the rated speed depend not only on the type of pump but also on the fluid used, the forepressure prevailing, the boiler input and the temperature of the water jacket. Ideally, all these factors should be specified when a speed-pressure characteristic is recorded.

The curves shown in Fig. 2.25 for a representative series of diffusion pumps from various manufacturers are typical.

It is largely because the speed is independent of the fine-side pressure over the working range that this type of characteristic is the one usually given. Such information also enables the pressure-time characteristic of the pump (for a given volume of the vacuum tank) to be determined. In practice, however, it is not usually possible to work out by simple calculation the time required for the diffusion pump to evacuate a vacuum tank of known volume between two pressure values, especially if the low pressure required is near the ultimate. Times required in practice are invariably longer than the calculated times because of the not easily estimated effects of out-gassing of the vacuum tank walls and of sealing materials. A rough working rule when evacuating a

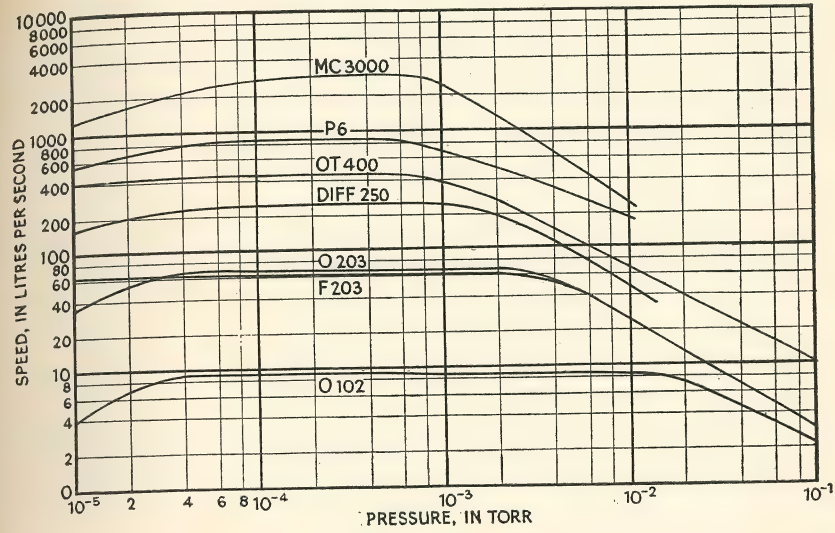


FIG. 2.25 Speed against pressure characteristics of various diffusion pumps

(Pump unbaffled; typical results are given; speeds will depend to some extent on the boiler heater wattage and the pump fluid used)

MC 3000: Consolidated Electrodynamics oil diffusion pump, 14-in. I.D. intake port, Octoil S
P6: Vacuum Industrial Applications oil diffusion pump, 6½-in. I.D. intake port, Silicone 703
OT 400: Leybold oil diffusion pump, 5 in. I.D. intake port, Leybold oil F
DIFF 250: Balzers oil diffusion pump
O 203: Edwards High Vacuum Ltd. oil diffusion pump, 2¼-in. I.D. intake port, Silicone 702
F 203: self-purifying version of O 203 (*see* Fig. 2.22)
O 102: Edwards High Vacuum Ltd. oil diffusion pump, 1-in. I.D. intake port, Silicone 702

sensibly leak-free container is to choose a diffusion pump with a speed of *n* litre per sec for a chamber of volume *n* litres.

Characteristics showing throughput (or mass-throughput) against pressure are gaining favour chiefly because they lead to ready assessment of the correct choice of fore-pump. This is especially recommended practice for large-scale vacuum plant in which a diffusion pump may be backed by a vapour ejector pump (§ 2.18) or a Roots pump (§ 2.7). The conversion of a volumetric speed against pressure characteristic to a throughput and also a mass-throughput characteristic is best illustrated by an example.

Consider a Leybold oil-diffusion pump, model OT 400. Values of the volumetric speed in litre per sec are given at various pressures in Table 2.5; the corresponding graph is shown in Fig. 2.26(*a*).

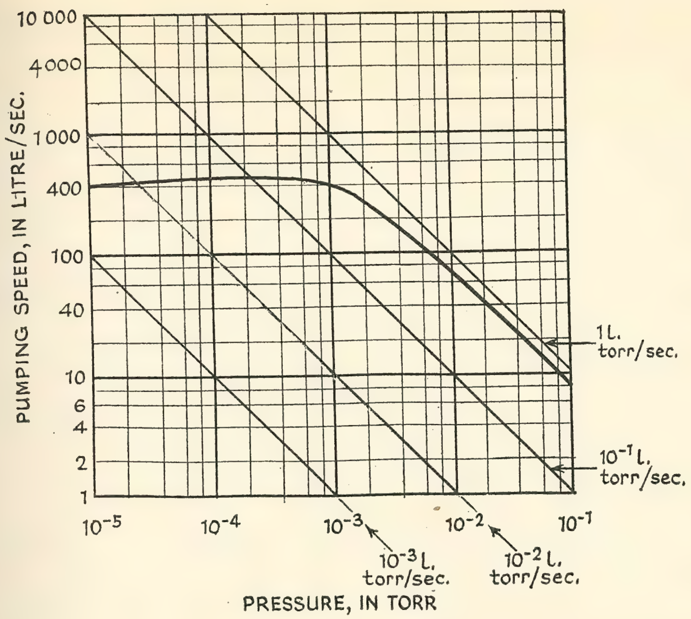
TABLE 2.5

Pressure in torr	Volumetric speed in litre/sec	Throughput in litre-micron/sec	Mass throughput in gram/sec
10^{-5}	400	4	$6{\cdot}32 \times 10^{-6}$
10^{-4}	450	45	$7{\cdot}1 \times 10^{-5}$
10^{-3}	400	400	$6{\cdot}32 \times 10^{-4}$
4×10^{-3}	160	640	1×10^{-3}
10^{-2}	70	700	$1{\cdot}1 \times 10^{-3}$
4×10^{-2}	20	800	$1{\cdot}27 \times 10^{-3}$
10^{-1}	9	900	$1{\cdot}42 \times 10^{-3}$

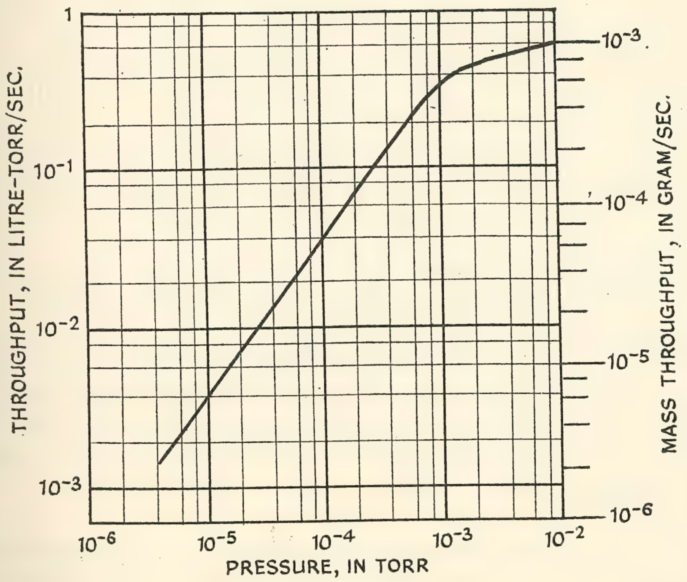
The third column of Table 2.5, headed *Throughput in litre-micron per sec* (1 litre at one micron pressure in one second is known as 1 **lusec**) is obtained from the second column, headed *Volumetric speed in litre/sec*, on the basis that this second column of figures is concerned with the *volume measured at the prevailing fine-side pressure* (first column), whereas the third column of figures is concerned with the *volume measured at a pressure of one micron, irrespective of the fine-side pressure*. At 10^{-5} torr, the volumetric speed is 400 litre per sec; at one micron (1 μ), this volume would be (from Boyle's law) $\frac{10^{-5}}{10^{-3}} \times 400$, *i.e.* 4 litres. Hence the figure appropriate to the first row of column three is 4 litre-micron per sec. Likewise, at 10^{-4} torr, the volumetric speed is 450 litre per sec, whereas at a pressure of one micron it will be 45 litre. It is a simple matter to deduce similarly all the figures in the third column. The determination of the mass-throughput in gram/sec then follows readily if the gas concerned is known. If air is being pumped, one litre at 760 torr and 20° C has a mass of 1·2 gram. At a pressure of one micron, the mass of a litre of air at 20° C will therefore be 1·2/760,000 gram, *i.e.* 1·58 microgram. The figures in column four—headed *Mass throughput in gram per sec*—are therefore obtained by multiplying the figures of the third column by $1{\cdot}58 \times 10^{-6}$.

The characteristics throughput against pressure and mass-throughput against pressure are given in Fig. 2.26(*b*).

An indication of the throughput per sec of a pump can also be given on the



(*a*) Volumetric speed against pressure characteristic for the Leybold OT400 diffusion pump with superimposed throughput against pressure lines



(*b*) Throughput and mass-throughput against pressure characteristics for the OT400 diffusion pump

FIG. 2.26

volumetric speed against pressure curves by superimposing on the same set of speed and pressure axes a series of parallel straight lines, at an angle to the axes, representing certain throughputs. For example, on the characteristics of the Leybold OT 400 pump (Fig. 2.26(*a*)), a series of straight lines representing throughputs of 10^{-3}, 10^{-2}, 10^{-1} and 1 litre-torr per sec are superimposed.

One of the merits of throughput pressure characteristics is illustrated by Fig. 2.27, for the National Research Corporation oil diffusion pump NRC B-4, type 01-0430-11. This pump is backed by a mechanical rotary pump: Kinney VSD-556. At the operating forepressures that the Kinney pump provides, it is seen that its throughput is, for all values of the fine-side pressure, equal to that of the diffusion pump. There is, consequently, no accumulation of gas in the system; the forepressure required is maintained throughout.

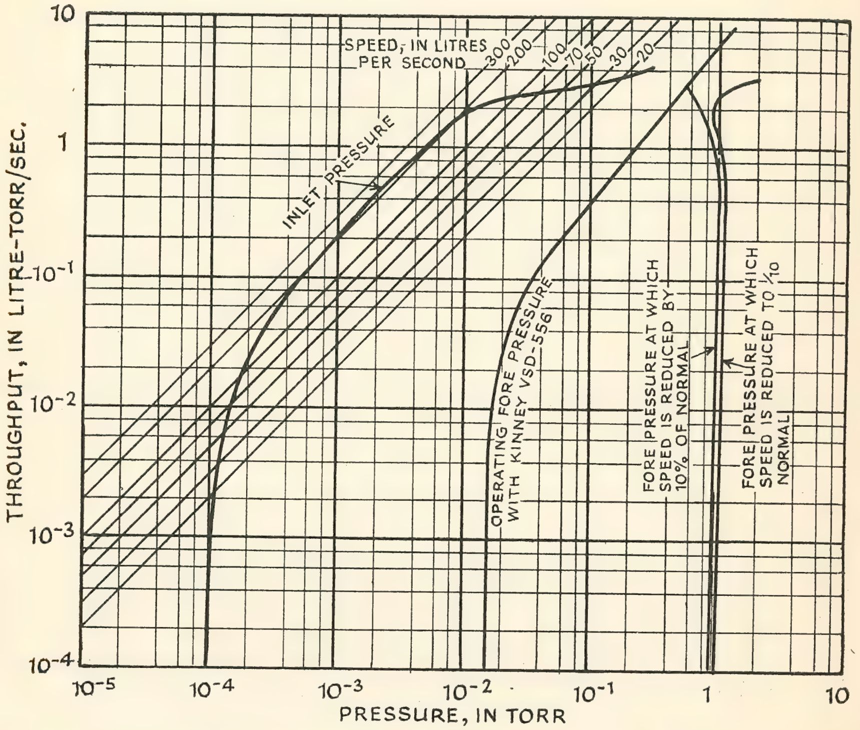


FIG. 2.27 Throughput against pressure characteristics for a NRC B-4 oil diffusion pump with a Kinney VSD-556 as a fore-pump

2.18. Ejector Pumps

On considering typical volumetric speed against pressure characteristics for diffusion pumps and for mechanical rotary pumps, it is seen that, in the region of 10^{-2} torr, both these classes of pump have low speeds compared with the values that prevail over their best operating regions. There is consequently a need for a type of pump which has high speed in the region about 10^{-2} torr. This need is fulfilled by pumps of the ejector class which employ either oil or mercury as the pump fluid. In this region, the ejector pump competes with the Roots pump (§ 2.7).

There are strictly two main types of oil ejector pump, though a distinction is not always made. The ejector pump proper is designed to provide large speeds at intake pressures greater than 2×10^{-2} torr, with a maximum speed often at about 10^{-1} torr, and to work relative to a forepressure exceeding 5×10^{-1} torr. The booster pump has a maximum speed at 10^{-3} to 10^{-2} torr, and is used as an intermediary in series between a large oil diffusion pump and the mechanical rotary pump.

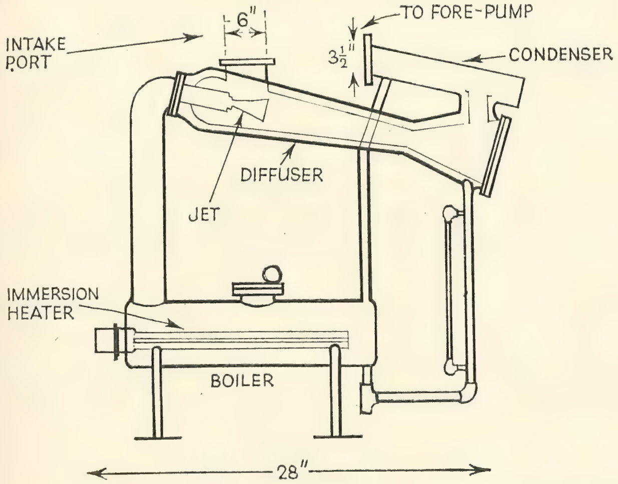


FIG. 2.28. Outline diagram of an oil vapour ejector pump

Jaeckel and Nöller (JN1) point out that if it is required to perform an industrial vacuum process in which considerable gas and vapour is evolved then, to work at a pressure of 0·1 torr as against 1 torr, would require an increase in size of the mechanical pump of ten times. Furthermore, if considerable vapour has to be removed which, at room temperature, has a vapour pressure of a few torr (*e.g.* organic vapours), it would become dissolved in the oil of a mechanical pump and the ultimate would be decided by the prevailing vapour pressure. For large quantities of such vapour, neither gas-ballasting nor oil-stripping (§ 2.5 and § 2.6) is effective. If a diffusion pump is used, it supplies the vapour to the mechanical fore-pump, the vapour pressure of the fore-pump oil is increased inordinately by the resulting contamination, and the forepressure to the diffusion pump will rise so much as to stop it working effectively. In such cases, the oil ejector pump is the recommended practice.

Compared with the diffusion pump, the ejector has an intake port of relatively small admittance area, the boiler pressure is considerably higher, and the jets supply a dense stream of vapour in which the molecules travel towards the forepressure region at initially supersonic velocities so that a large pressure drop across the jet is provided to permit a high forepressure tolerance. The gas molecules reach the vapour stream of an ejector pump by viscous flow, the mean free path (order of 10^{-2} to 10^{-4} cm) being considerably less than the nozzle clearance at the prevailing intake pressures. Consequently, the pump speed is greatly influenced by the intake pressure.

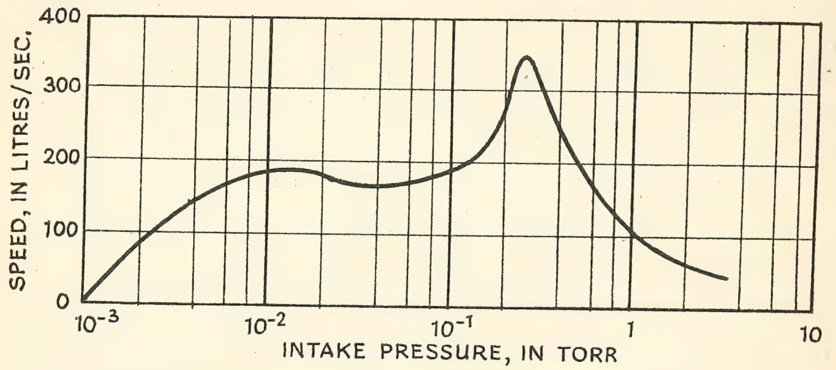


FIG. 2.29 Pumping speed against intake pressure characteristic for KB300 oil vapour ejector pump. Heater wattage: 3000

The design of a typical oil vapour ejector pump is illustrated schematically in Fig. 2.28 (Consolidated Electrodynamics Corporation model KB300, *see also* Gerow, G3). Vapour from the oil, heated in the boiler, rises to the hydrodynamically-designed (Laval) jet which it leaves with initially supersonic velocity to entrain the gas coming in from the intake port of the pump. This gas is compressed as it passes down the converging diffuser cone by a ratio of the order of 10. The oil vapour condenses on the cooled walls of the diffuser and in the condenser between the ejector pump and the mechanical backing pump. For this pump, the intake pressure may range from $2{\cdot}5 \times 10^{-2}$ to 7×10^{-1} torr and the limiting forepressure from 5×10^{-1} to 10 torr, though

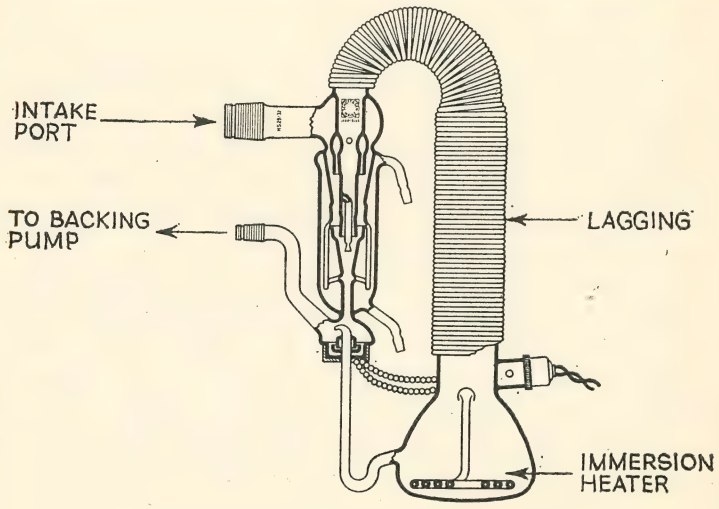


FIG. 2.30 Glass oil vapour ejector pump

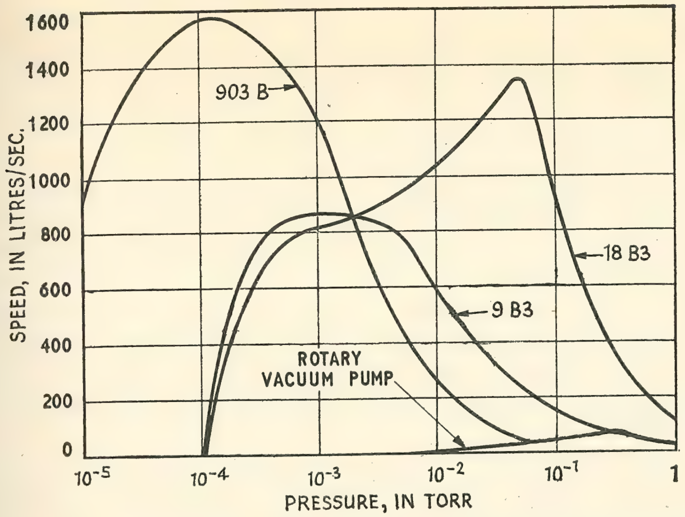


FIG. 2.31 Speed against pressure characteristics of oil-vapour ejector pumps 9B3 and 18B3, oil-diffusion pump 903B and mechanical rotary pump of displacement 100 cu ft per min

3 torr is usually the upper limit. The pumping speed against intake pressure characteristic for this pump is shown in Fig. 2.29.

A wide range of sizes of oil ejector pumps is available commercially: Fig. 2.30 shows a glass oil ejector pump which has a speed of 4 litre per sec at 10^{-1} torr (heater wattage: 550) made by Jena Glaswerk; Plate 3 depicts the 18B3 oil vapour ejector pump with a peak speed of 1300 litre per sec at 8×10^{-2} torr at a heater wattage of 6·4 kW (Edwards High Vacuum Ltd.).

Fig. 2.31 gives speed-pressure characteristics of the Edwards High Vacuum Ltd. 9B3 and 18B3 oil ejector pumps compared with that of a 903B oil diffusion pump and also that of a mechanical rotary pump with a free air displacement of 100 cu ft per min.

If a supply of high pressure steam (pressure about 60 lb/sq in.) is available, the **steam-ejector pump** offers notable advantages for producing a rough vacuum in a system, especially one of several hundred cubic feet in volume. A four-stage steam ejector will produce a minimum intake pressure of about 0·5 torr with the discharge to the atmosphere; a five-stage arrangement with inter-stage water-cooled vapour condensers can be used

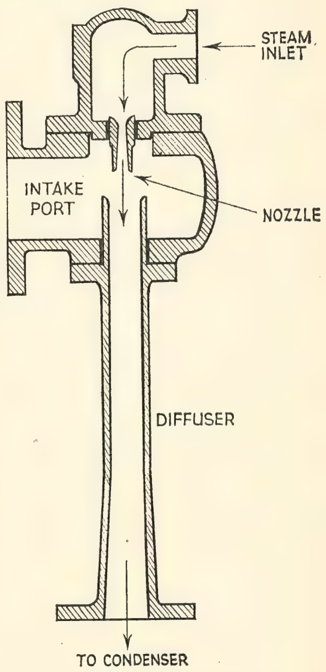


FIG. 2.32 Single-stage steam ejector pump

to produce a pressure of about 3×10^{-2} torr. The outstanding advantage is that this is the *only* type of pump able to handle all kinds of vapours and is consequently of especial interest in several chemical operations, especially those involving the pumping of condensable (and, particularly, corrosive) vapours at total gas pressures above 0·5 torr.

In the single stage of a steam-ejector (Fig. 2.32) a high velocity jet of steam is discharged through the nozzle into a convergent-divergent diffuser and entrains gases and vapours entering the pump intake port. This entering gas and vapour has imparted to it the velocity of the steam (which is thereby decelerated) towards the discharge outlet. In a single stage, the discharge to intake pressure ratio possible is about 7·5. A typical steam ejector (Mirrlees Watson Ltd.) will pump about 5 lb of gas per hour, corresponding to a speed of 30,000 cu ft per hour at 0·5 torr for a vapour of molecular weight 100 (Dushman, D1).

For further information on steam ejector pumps, their correct arrangement with inter-stage condensers and their performances, see Blatchley (B3), Morse (M1), Stinson (S4), Royds and Johnson (RJ1) and Fondrk (F2).

3

VACUUM GAUGES

3.1. Classification of Types

Several texts give detailed descriptions of the various methods of measuring low gas pressures (Dushman, D1; Guthrie and Wakerling, GW1; Jaeckel, J1; Pirani and Neumann, PN1; Reimann, R3; Yarwood, Y1). Recently Leck (L3) wrote a monograph which deals with the theory, practice and design of gauges. The present survey does not aim to be comprehensive but rather to classify the various types of gauge, compare and contrast them, consider special points, particularly with regard to correct usage, and discuss recent developments.

Table 3.1 is a classification of the vacuum gauges according to the physical principle of operation involved; Fig. 3.1 gives the pressure ranges of the models frequently employed.

The following sections relate to the categories of Table 3.1.

3.2. Gauges in which the Pressure of Gas is Directly Balanced Against a Head of Liquid

These gauges provide absolute methods of measurement of the total gas pressure independently of the nature of the gas. Designs of suitable mercury and oil manometers are illustrated in Fig. 3.2.

Important points to watch are:

(*i*) Cleanliness of both liquid (mercury or oil) and glass is essential, otherwise inaccuracies arise due to 'sticking' (*see* § 3.4 concerning the cleaning of glass). Rinsing the tube for a few hours with hydrofluoric acid vapour is recommended to prevent sticking.

(*ii*) Using mercury, the limit of accuracy of *reading* is 1 torr with direct observation. Use of a cathetometer enables readings down to 0·1 or even 0·05 torr to be made.

(*iii*) The lowest *recordable* pressure if a mercury manometer is used is 1 torr (assuming a permissible max. error of ±10%).

(*iv*) A differential manometer (Fig. 3.2(*b*)) is preferable to the straight pattern of Fig. 3.2(*a*) because the latter demands correction for the barometric height.

(*v*) Many gases and vapours react with mercury, *e.g.* chlorine, bromine, hydrochloric acid gas. Even exposure to air causes slight oxidation of the mercury which leads to 'sticking'.

(*vi*) The vapour pressure of mercury ($1{\cdot}3 \times 10^{-3}$ torr at 20° C) is exerted.

TABLE 3.1
Classification of vacuum gauges

Physical Principle Involved	Gauges Available
Pressure of gas balanced against head of liquid	Mercury manometer; oil manometer; Dubrovin gauge
Pressure of gas balanced against mechanically exerted pressure	Bourdon gauge; aneroid capsule type; bellows manometer; devices for measuring low vapour pressures employing membranes, thin glass spirals; also where the gas pressure is balanced against forces exerted by gravitation or magnetically
Gas volume reduced to increase pressure by a known ratio. Resultant increased pressure balanced against a head of liquid	McLeod gauge; the vacustat; these gauges with oil instead of mercury
Measurement of rate of transfer of molecular momentum from a hot to a cold surface	Knudsen gauge; Gaede molvakuummeter
Variation of the thermal conductivity of a gas with pressure at low pressures	Hot wire gauges of the Pirani and the thermocouple type. The thermistor gauge
Variation of the viscosity of a gas with pressure at low pressures	The decrement gauge
Indicator gauges depending on the variation of the form of a gaseous discharge with pressure and of its colour with the nature of the gas	The discharge tube. Use of the Tesla coil; discharge tubes of special design employing fluorescent screens, *e.g.* the Skanascope
Measurement of the ionization currents in the residual gas	Three types: (*i*) the gas is ionized by thermionically emitted electrons accelerated through a p.d., *i.e.* the hot cathode ionization gauge; (*ii*) gas ionized by electrons formed in a cold discharge and electron paths from cathode to anode are increased by use of a magnetic field which introduces oscillations and spiralling of the electrons, *i.e.* the Penning (Philips) gauge; (*iii*) the gas is ionized by α-particles emitted from a radioactive source, *i.e.* the alphatron gauge
Measurement of ionization currents due to selected constituent gases present	The mass spectrometers and the omegatron are capable of recording the partial pressures of the various gases present in the residual vacuum

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The use of a low vapour pressure oil (*e.g.* dibutyl phthalate or Apiezon oil) on the surface of the mercury helps to prevent mercury vapour from affecting mercury-sensitive materials in the vacuum system (Fig. 3.2(*a*)).

(*vii*) To reduce the effects of surface tension and irregular light refraction in the glass tube, Leck (L3) recommends the use of thin-walled tubes not less than 1 cm diameter.

The use of oil in place of mercury is attractive because the specific gravities of most low vapour pressure oils at room temperature are about 1 (Table 2.2) compared with 13·6 for mercury. Hence, reading of the oil level to 0·1 mm (using a cathetometer) gives an accuracy of pressure reading to 7×10^{-3} torr. The lowest satisfactorily recordable pressure is about 5×10^{-2} torr. A more sensitive type, the Backovsy–Slavik inclined butyl-benzyl phthalate manometer, is described by Jnanananda (J3).

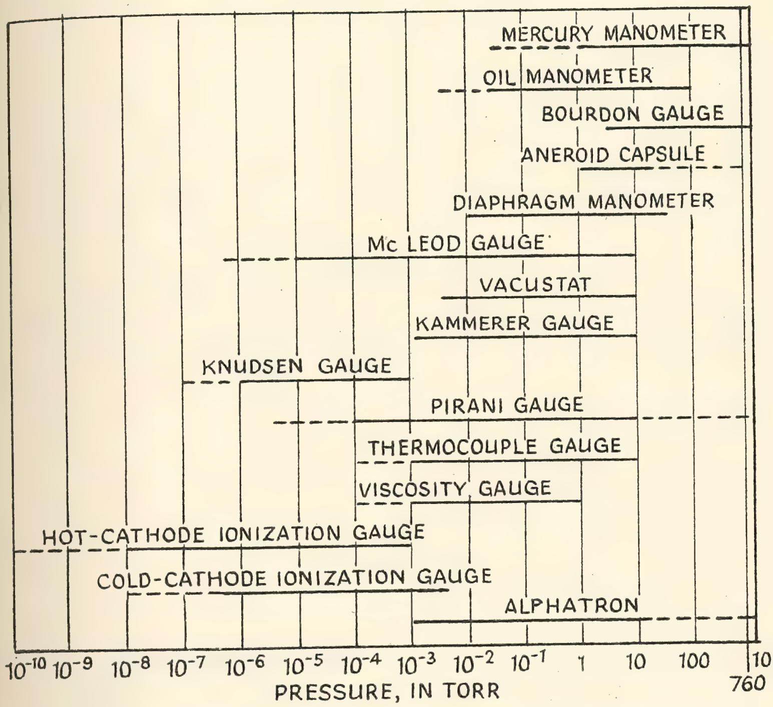


FIG. 3.1 Pressure ranges of vacuum gauges (full lines show the ranges of the commercially available models; the dotted line extensions indicate the extreme limits of the pressure ranges which can be achieved by special design)

Difficulties in the use of oil. (*i*) Oils contain much dissolved air. This is released in practice by heating the oil in the manometer whilst it is undergoing pumping for about 30 min before use. As far as possible, the oil manometer should not then be re-exposed to air at atmospheric pressure. Small quantities of dissolved gas inevitably remain; occasional evolution of a gas bubble during a pressure measurement ruins the recording.

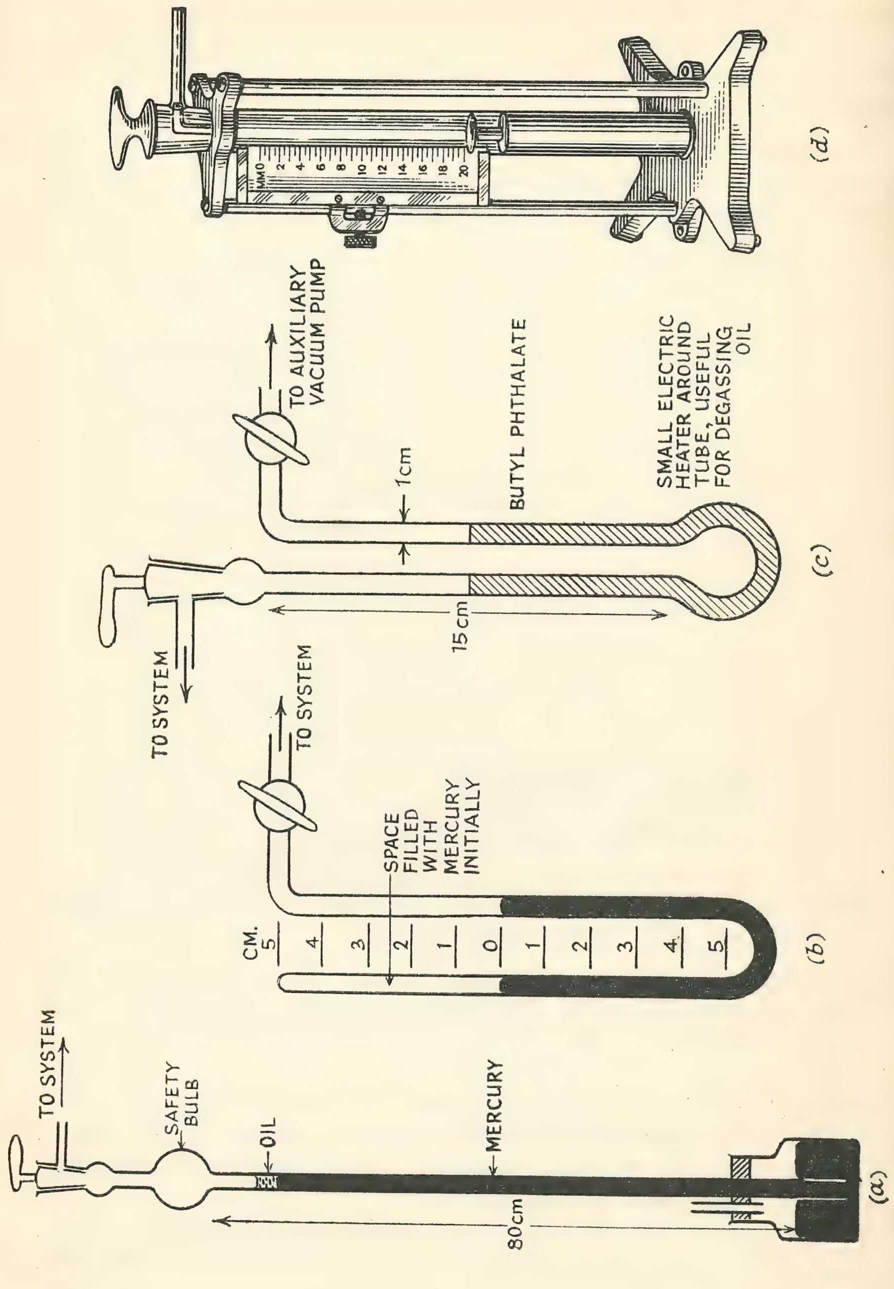


FIG. 3.2 Mercury and oil manometers

(*ii*) Oils 'wet' glass. Butyl phthalate is most free from this objection, but Apiezon and silicone oils have been used.

(*iii*) Oils dissolve and/or react with some gases and vapours.

The best method of using an oil-filled manometer for recording the range of pressures from 5×10^{-2} to 5 torr is illustrated by Fig. 3.2(*c*).

Liquid-filled manometers are used chiefly in gas-filling procedures, *e.g.* in the manufacture of gas-filled discharge lamps, electron tubes, Geiger counters, etc. The mercury manometer in the form of a small U-tube attached to the fore-pump of a vacuum system can be a useful indicator and warning device. The danger of an in-rush of gas ejecting the liquid from the manometer has led to the preferred use of the aneroid capsule and the bellows manometer in many cases of industrial practice.

A useful commercially available device is the **Dubrovin gauge** of the Welch Scientific Company. It employs an evacuated metal tube which floats vertically in mercury in a cylindrical glass vessel connected to the vacuum system (Fig. 3.2(*d*)). The top of this metal tube is firmly closed by a flat metal disc whilst the bottom end, in the mercury, is loosely closed by a glass sphere. The height of the flat-top cover disc indicates the gas pressure above the mercury against a scale engraved on the glass cylinder. When the pressure is reduced, the metal tube will float higher, and vice versa. Models with a 6 : 1 and a 9 : 1 magnification over that obtained by direct reading of the mercury level are available.

Many devices have been developed for increasing the accuracy with which the difference in levels in a mercury-filled U-tube manometer can be determined. These methods are surveyed by Pirani and Neumann (PN1) and more extensively by Dushman (D1). They include a tilting form of manometer with a sensitivity of 10^{-3} torr due to Lord Rayleigh (R5), the use of optical-lever methods, providing a sensitivity of 10^{-3} torr, by Schrader and Ryder (SR1) and by Carver (C2) who claims a sensitivity of 10^{-4} torr. Further methods are recommended by Newbury and Utterback (NU1), Johnson and Harrison (JH1), Pearson (P1) and Hickman (H3); electrical methods of indication have been designed by Klumb and Haase (KH1), Simon and Fehér (SF1) and Hawkins (H4). These devices are used mostly in research, especially for the recording of moderately low vapour pressures.

3.3. Pressure of Gas Balanced Against a Mechanically Exerted Pressure

The two main classes of instrument are:

(*i*) Gauges which utilise (*a*) the Bourdon gauge principle (*b*) an aneriod capsule (*c*) metal bellows, and (*ii*) specialized pieces of apparatus for the direct measurement of vapour pressures.

(*i*) **The Bourdon gauge** gives pressure readings over the range up to 760 torr, but is unreliable below 5 torr and usually has a calibration dependent upon the external atmospheric pressure. However, Holland–Merten (H5) describes a 'Barovakuummeter' of the Bourdon type incorporating an aneroid capsule to provide correction against variations of the barometric height. An unusual feature of this instrument is that the *scale* moves in indicating the pressure, and not the pointer. Barometrically compensated **aneroid capsule gauges** are reliable over the range from 1 to 20 torr. Fig. 3.3 illustrates a pattern supplied by Edwards High Vacuum Ltd.

Both these types of instrument are robust with direct dial reading of the pressure; they are easily attached to a metal vacuum system and give readings independent of the nature of the gas. The gas is not in contact with glass or liquid, but the metal parts used are subject to attack by some vapours.

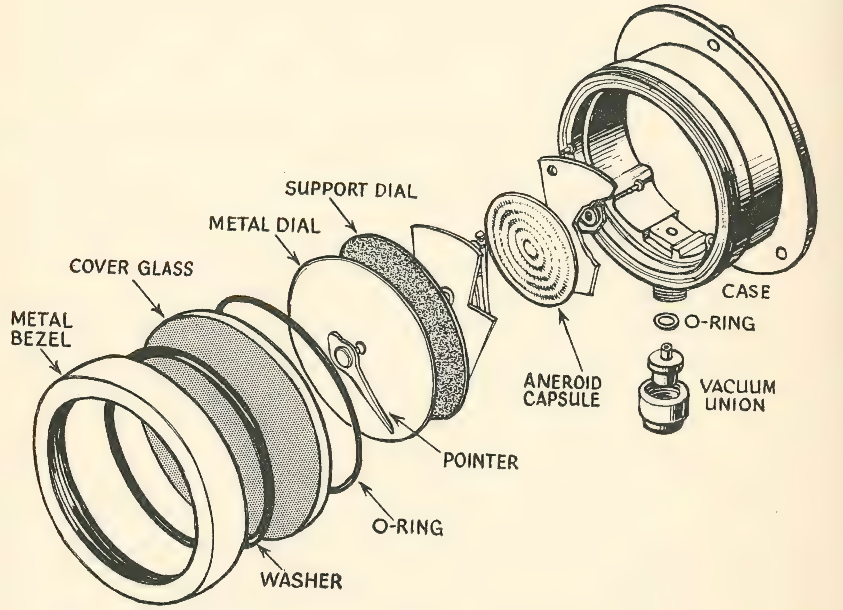

SUPPORT DIAL
METAL DIAL
COVER GLASS
METAL BEZEL
CASE
O-RING
ANEROID CAPSULE
VACUUM UNION
POINTER
O-RING
WASHER

FIG. 3.3 A barometrically compensated aneroid capsule manometer (exploded view based on a diagram supplied by Edwards High Vacuum Ltd.)

Ladenburg and Lehmann (LL1) describe a Bourdon-type manometer which employs a glass spiral with attached mirror and is useful for measuring the vapour pressures of active gases; in particular, it was employed to measure the dissociation pressures of chlorides and registered a pressure of a fraction of a torr of chlorine.

Alpert, Matland and McCoubrey (AMM1) describe an instrument which makes use of a liquid manometer for absolute calibration but uses a metallic diaphragm as the pressure-sensitive element in contact with the gas (Fig. 3.4). This enables the vacuum system to be thoroughly degassed by baking before introducing gas samples into it. A Kovar cup is connected to the vacuum system. Across this cup, a thin corrugated metallic diaphragm is silver-brazed which isolates the region *A*, in contact with the vacuum system, from the region *B* in which the gas pressure is recorded by the manometer. If the diaphragm is undeflected, the pressure in *A* equals the pressure in *B*. This null position is recorded by measurement with an a.c. bridge of the electrical

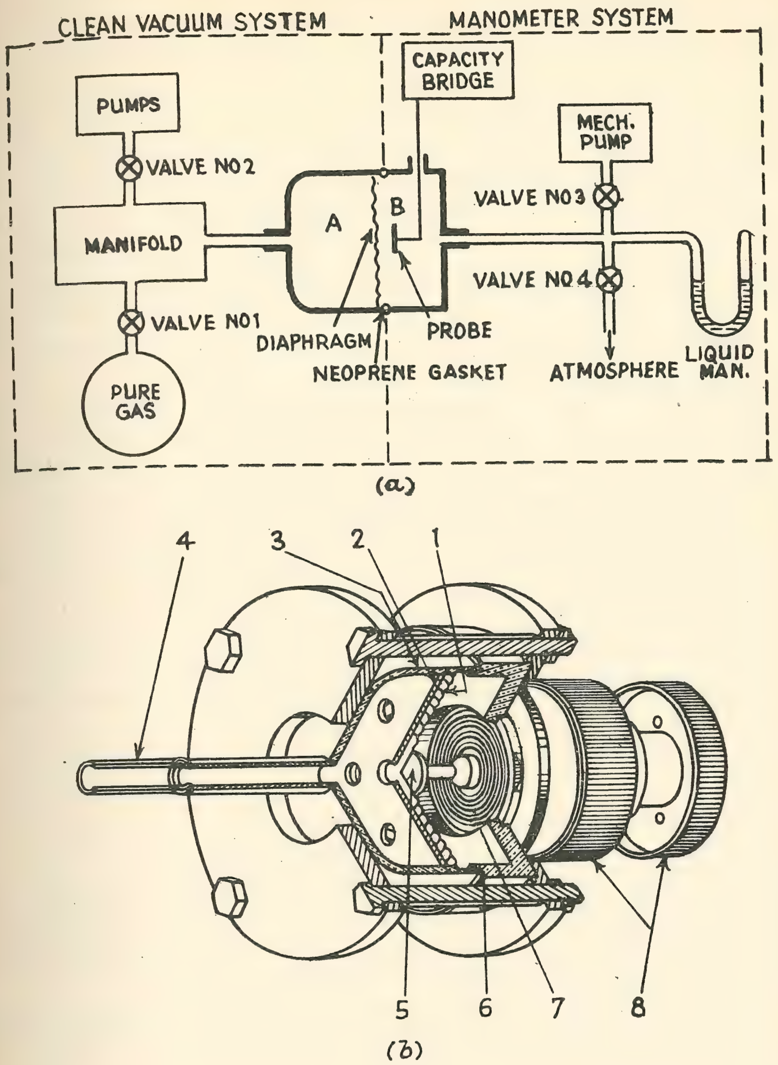

CLEAN VACUUM SYSTEM
MANOMETER SYSTEM
CAPACITY BRIDGE
PUMPS
MECH. PUMP
VALVE NO 2
VALVE NO 3
A
B
MANIFOLD
VALVE NO 4
VALVE NO 1
PROBE
DIAPHRAGM
NEOPRENE GASKET
ATMOSPHERE
LIQUID MAN.
PURE GAS
(a)
4
3
2
1
5
6
7
8
(b)

FIG. 3.4 Absolute manometer (*Alpert, Matland and McCoubrey*)

1, Pressure-sensitive diaphragm; 2, backing-plate of $\frac{1}{16}$ in. Kovar perforated sheet; 3, Kovar cup—0·10 in. wall thickness; 4, Kovar-to-glass tubing; 5, capacitative probe—$\frac{1}{2}$-in. dia brass disc mounted on Mycalex post; 6, Neoprene gasket; 7, Kovar diaphragm—0·01 in. thick; 8, differential screw for adjusting probe position capacitance of the diaphragm relative to an inserted metal probe. In use, the probe is first removed and the Kovar cup is sealed by a clamped-on, flat copper plate. The vacuum system is then pumped out and baked at 400 to 500° C. To prevent undue deflection of the diaphragm at this high temperature, the region *B* of the Kovar cup is meanwhile evacuated by a mechanical rotary pump. The probe is re-inserted, the gas sample introduced into the clean vacuum system and air admitted to the region *B* until the diaphragm deflection is zero. The gas pressure in the system then equals the pressure of the air in the isolated region *B*, and this pressure is recorded by the liquid manometer. It is claimed that the method facilitates the production of vacua of 10^{-9} torr, subsequent introduction of pure gas samples up to 50 torr and accurate recording of the latter pressures within 0·1 torr, if an oil manometer is used. The maximum error introduced by the flexible diaphragm is 10^{-2} torr. The diaphragm undergoes a movement of 3×10^{-4} in. for a pressure difference of 1 torr across it.

Lorant (L4) describes a diaphragm-type manometer which covers the range from 10^{-3} to 10^{-1} torr with a sensitivity of 10^{-4} torr. Two coils are arranged near the corrugated diaphragm, one coil is energized by high frequency a.c. and induces an e.m.f. in the other. The magnitude of this induced e.m.f. depends on the movement of the membrane under the pressure of gas within the gauge. The electrically indicated readings are directly proportional to the gas pressure.

Utilizing bellows of Tombac or beryllium-copper, East and Kuhn (EK1, Y1) have developed a direct-reading manometer where pressure differences down to 10^{-2} torr are recorded in terms of the deflection of a spot of light on a scale.

Gauges of these types—other than the Alpert instrument—are not absolute because in general it is not possible to determine readily the pressure of the gas in terms of the geometrical and physical constants of the gauge. They must, therefore, be calibrated against a mercury manometer or a McLeod gauge. The calibration is, however, independent of the nature of the gas. They form practical substitutes for liquid-filled manometers with the advantages of compactness, avoidance of liquid and glass, direct dial reading and virtually instantaneous pressure recording.

(*ii*) Sensitive but delicate apparatus for the **direct measurement of vapour pressures** down to 10^{-5} torr or even 10^{-6} torr. The principle involved is to maintain the substance of which the vapour pressure is required in a glass or fused silica container at a known temperature. This container, which is pumped free of air, is separated from the high vacuum in a surrounding vessel by a close-fitting lid or membrane of known area placed over an orifice. The forces acting on this lid are then those due to the vapour pressure of the enclosed substance. These forces attempt to push the lid away from the orifice, so a restraining force is adjusted to restore equilibrium, *i.e.* keep the lid just closed. This restraining force is arranged to be provided by gravity (Verhoek and Marshall, VM1) or by a cantilever and a magnetic balance (Deitz, D3). Herlet and Reich (HR1) describe an attractive apparatus for measuring vapour pressures in the range from 10^{-7} to 10^{-2} torr (*i.e.* useful for measurements on pump oils) which employs the moving-coil mechanism of a sensitive microammeter to provide the restraining force.

The limitation to these direct mechanical methods of measuring vapour pressures is indicated by considering the small forces involved. A pressure of 10^{-3} torr corresponds to 1·333 dyne per cm^2 (Table 1.1). Therefore, if a pressure of $0{\cdot}75 \times 10^{-3}$ torr is exerted on a lid or membrane of surface area 1 sq cm it provides a force to be measured of 1 dyne *i.e.* 1 mg wt approx. To measure pressure by this means of 10^{-6} torr consequently demands the measurement of weights of the order of 10^{-2} mg, assuming a cover lid of area 10 cm^2 is used. The necessity for delicate apparatus is obvious.

3.4. Gas Volume Reduced to Increase Pressure by a Known Ratio

If a mercury manometer is able to record pressures to 1 torr, pre-compression of a volume of gas by a ratio of, say, 10^4 to 1 will enable gas pressures down to 10^{-4} torr to be registered. This principle is involved in the well-known McLeod gauge (Fig. 3.5(*a*)) (McLeod, M2; Leck, L3; Dushman, D1; Yarwood, Y1), in the swivel-type McLeod, *e.g.* the vacustat (Fig. 3.5(*b*)) (Flosdorf, F3; Leck, L3; Yarwood, Y1), which is similar to the Gaede vacuscope, and in the very convenient Kammerer gauge (*see also* Florescu, F4), (Fig. 3.6). The same principle could well be applied by using a piston to compress the gas and an aneroid capsule to record the increased pressure (Yarwood, Y1).

The outstanding advantages of the McLeod gauge are:

(*i*) It records absolutely the pressures of the permanent gases such as air, nitrogen, oxygen, hydrogen, carbon monoxide and the inert gases. Furthermore, calibration is readily carried out using the equation,

$$p = \frac{v}{V} h^2 \tag{3.1}$$

where p is the gas pressure to be recorded in torr, v is the volume of 1 mm length of the closed capillary and V the volume of the bulb plus capillary, both these volumes being given in mm^3, whilst h is the length in mm of the compressed gas between the top of the inside of the closed capillary at *A* and the level of the mercury at *B* in this capillary, when the level of the mercury in the comparison capillary is raised to the same height as *A* (Fig. 3.5(*c*)).

The McLeod gauge is the only readily constructed instrument which records absolutely pressures below 10^{-3} torr. It is therefore usual practice to calibrate other gauges against the McLeod.

(*ii*) If the services of a skilled glass-blower are available the McLeod gauge can be made for the cost of a few shillingsworth of borosilicate glass, the necessary vacuum taps and—the most expensive item—the mercury.

The chief difficulties involved are:

(*i*) In compressing the gas by a high ratio, the condensable gases, *i.e.* those with a critical temperature above room temperature, may be liquefied. Moreover, even if such gases do not liquefy, Boyle's law is not obeyed, and this law is assumed in calculating the pressure increase resulting from the compression. Water vapour in air is the most common source of error here.

(*ii*) Errors are introduced due to capillary depression and the difficulty of (*a*) obtaining a closed capillary with an accurately uniform bore (*b*) sealing-off the top of this capillary so as to provide a flat end. These factors are discussed fully by Leck (L3) who shows that a possible error of $\pm 100\%$ at 5×10^{-6} torr and $\pm 10\%$ at 5×10^{-4} torr may be obtained even in a well-designed thoroughly clean gauge. These possible errors are too frequently overlooked in using the McLeod to calibrate other gauges, *e.g.* the hot-cathode ionization gauge (§ 3.9).

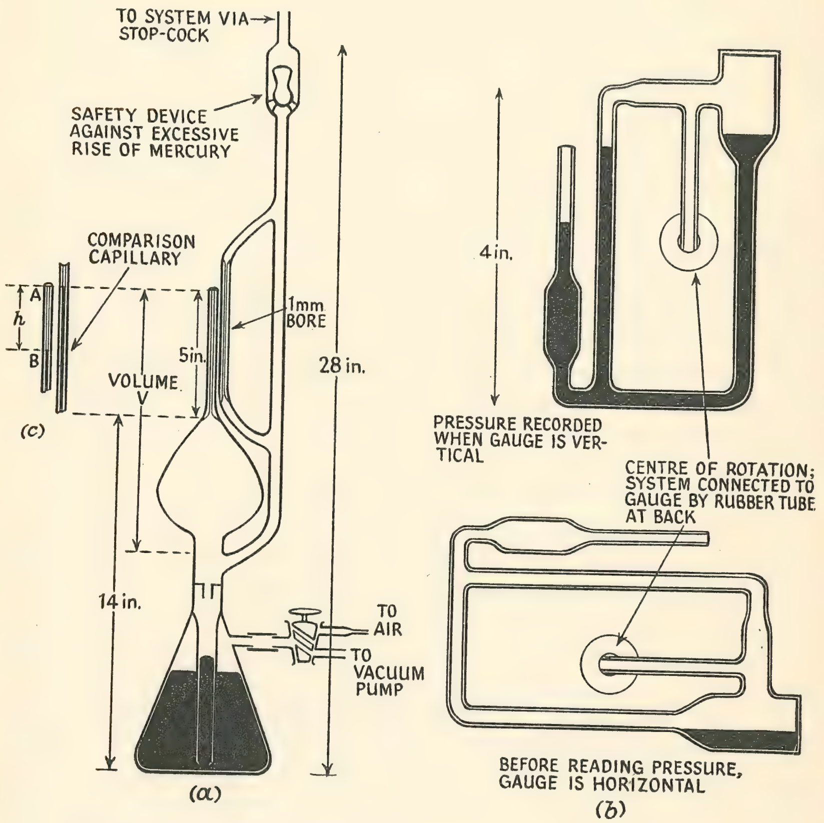

TO SYSTEM VIA STOP-COCK
SAFETY DEVICE AGAINST EXCESSIVE RISE OF MERCURY
COMPARISON CAPILLARY
A
h
B
(c)
5in.
VOLUME V
1mm BORE
28 in.
14 in.
TO AIR
TO VACUUM PUMP
(a)
4 in.
PRESSURE RECORDED WHEN GAUGE IS VERTICAL
CENTRE OF ROTATION; SYSTEM CONNECTED TO GAUGE BY RUBBER TUBE AT BACK
BEFORE READING PRESSURE, GAUGE IS HORIZONTAL
(b)

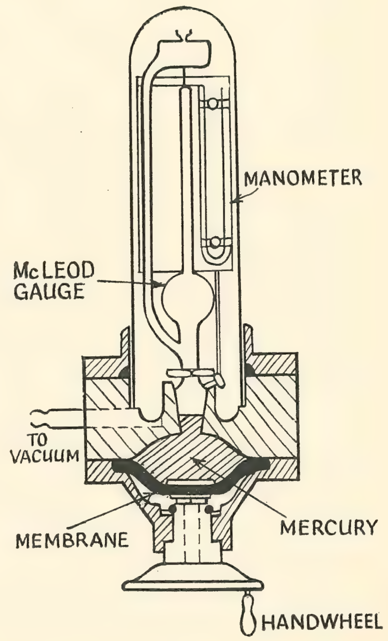
FIG. 3.5 Two forms of the McLeod gauge (*a*) shortened model; (*b*) the Vacustat

(*iii*) The time involved in pre-compressing the gas (about 1 min in practice) means that instantaneous pressure readings are impossible. This difficulty is aggravated by the time taken for the gas in the gauge to become in pressure equilibrium with the gas in the vacuum tank, because of the impedance to gas flow of the long connecting tubing necessary.

(*iv*) The McLeod gauge is bulky and somewhat fragile.

(*v*) The use of mercury means that a vapour pressure of about 10^{-3} torr is present at room temperature. This can be avoided by the use of a cold trap (§ 2.11).

Factors in the design and operation of the McLeod gauge. It is readily seen from equation (3.1) that the recording of the lowest pressures demands a large capacity bulb and a capillary of small diameter. The bulb volume is not conveniently greater than 300 cu cm or possibly 500 cu cm (the mass of 500 cu cm of mercury if 6·8 kg, *i.e.* nearly 15 lb!). Haase (H6) has, nevertheless, used a bulb of 1400 cu cm, supported by a close-fitting mould of plaster of Paris. The capillary inside diameter cannot be less than 0·5 mm and is preferably 1·00 mm, otherwise it is difficult to prevent the thread of mercury in it from breaking on lowering the mercury level. Haase recommends that capillaries of smaller diameter than 1 mm be ground internally by drawing a wire through them which is about two-thirds of the capillary diameter and fed with a fine abrasive such as alumina. Careful drawing and turning of the wire in the capillary is continued until the inner glass wall is no longer transparent. This practice considerably reduces the tendency of the mercury thread to break. Cleaning and slight etching of the inside walls of the capillaries with hydrofluoric acid is an alternative.


MANOMETER
McLEOD GAUGE
TO VACUUM
MEMBRANE
MERCURY
HANDWHEEL

To make a pressure reading, handwheel is turned to left so membrane rises and forces mercury into McLeod gauge.

FIG. 3.6 The Kammerer gauge (*Courtesy of E. Kammerer*)

Presuming that the lowest pressure recordable with a McLeod gauge corresponds to a length of the compressed air in the closed capillary of 1 mm (*i.e.* $h = 1$ mm) and that the maximum length recordable, *i.e.* the total length of the capillary, is 100 mm, the graphs of Fig. 3.7 give the pressure ranges available using McLeod gauges of various values of v/V. An accurate assessment of the pressure from a reading of h of 1 mm demands that the top of the capillary is sealed off flat, that the gauge is carefully constructed using very uniform capillary tubes, and that the difference between the capillary depression when raising and lowering the mercury is assessed. Even so, errors of ±25% must be expected at the lowest pressures.

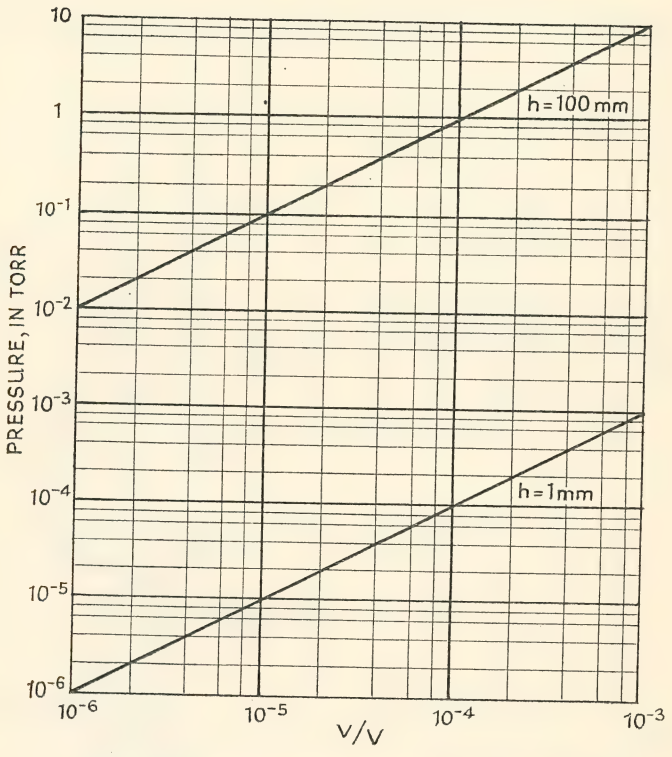


FIG. 3.7 Pressure ranges of the McLeod gauge

Modifications of the McLeod gauge to enable a wider range of pressures to be recorded (*i.e.* to increase the upper pressure limit) are described by Romann (R6, *see* Leck, L3) and Wyllie (W1).

According to Farkas and Melville (FM1) the pressures of *imperfect* gases can be estimated by means of a McLeod gauge. The equation

$$\frac{p_0 V_0}{p_1 V_1} = 1 + \lambda \tag{3.2}$$

is employed. This is the suitably modified form of Boyle's law where p_0 is a low pressure, V_0 the corresponding gas volume, p_1 is atmospheric pressure and V_1 the gas volume at atmospheric pressure. λ is a numerical constant depending on the nature of the gas and is given in Table 3.2.

TABLE 3.2

Gas	λ
CO_2, C_2H_2, C_2H_4, C_2H_6, H_2O	0·07
SO_2	0·0234
NH_3	0·015
PH_3	1600

Francis (F5) discusses the detection of the presence and estimation of pressures of condensable vapours using a McLeod gauge. Another method (Fig. 3.8) is to compress the mixture of permanent gas and condensable vapour into a length l of the closed capillary by a head of mercury of height h. Here h and l are not usually the same because the level in the comparison capillary is not, in general, brought opposite the top of the closed capillary. If v is the volume per unit length of the closed capillary then lv is the volume of the compressed gas–vapour mixture. If the gas were a permanent one, *i.e.* no vapour were present, Boyle's law would apply and

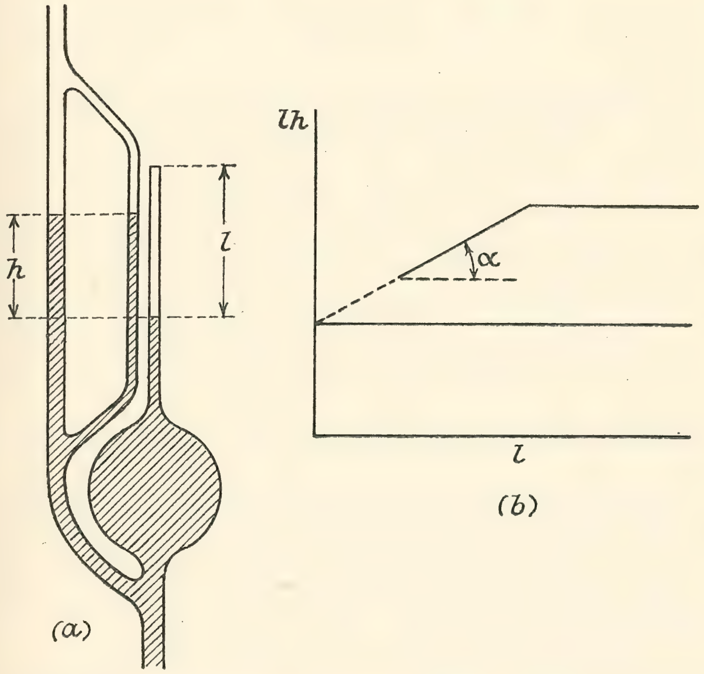


FIG. 3.8 Estimating condensable vapours by means of a McLeod gauge

$$lv = \frac{k}{p_g} \tag{3.3}$$

where p_g is the permanent gas pressure and k is a constant.

With a mixture of gas and vapour,

$$h = p_g + p_v \tag{3.4}$$

where p_g and p_v are the partial pressures of the gas and vapour respectively.

In the experiment, h is varied by altering the height of the mercury reservoir of the McLeod gauge and corresponding values of l are noted. lh is then plotted against l. With no condensable vapour present, or if the compression is insufficient to condense the vapour, the graph obtained is a straight line parallel to the l-axis. In the case of a gas–vapour mixture, as soon as condensation begins with sufficient compression, a straight line of angle of α to the l-axis is obtained, obeying the equation

$$lh = lp_g + lp_v \tag{3.5}$$

Determination of the angle α hence indicates the magnitude of the saturation vapour pressure p_v whilst extrapolation to $h = 0$ gives the permanent gas pressure p_g.

Cleaning a McLeod gauge. Preparatory to filling with distilled mercury and setting up, a McLeod gauge must be scrupulously cleaned. A recommended procedure is to clean with nitric acid, followed by ammonium hydroxide, distilled water and then alcohol. The alcohol can then be easily removed by passing clean, dry air through the gauge. A final cleaning with ether is *not* recommended because ether usually contains fats which contaminate the glass. After filling the gauge with mercury and sealing to the vacuum system, the lowest possible pressure is obtained and then the glass of the McLeod is baked with a flame to release any remaining condensable vapours, especially water vapour.

Oil-filled McLeod gauges have been constructed. The advantages afforded are:

(*i*) The specific gravities of low vapour pressure oils are about unity. For example, butyl sebacate is suitable as it gives comparative freedom from wetting of the glass and has a specific gravity of 0·92 (Table 2.2). Hence, the sensitivity of the gauge compared with that obtained using mercury is increased by $\sqrt{13{\cdot}6/0{\cdot}92}$, *i.e.* approx 4 times.

(*ii*) The gauge is much lighter in weight. Much less stress on the glass is therefore encountered on raising and lowering the liquid than if mercury is used. Furthermore, swivel-type McLeods (*e.g.* of the vacustat pattern) can be constructed with considerable bulb volumes.

(*iii*) Sticking of the liquid to the glass is avoided.

(*iv*) The low vapour pressure of the oil dispenses with the necessity for a cold trap.

The outstanding difficulty in using oil is that it evolves air and other dissolved gases. This practically prohibits its use in the usual pattern of McLeod gauge, though it has been utilized in the swivel-form (Guthrie and Wakerling, GW1) and in a compact form (Florescu, F6). It is essential to heat the oil *in vacuo* to release as much dissolved gas as possible before use in the McLeod and then warm the oil in the evacuated gauge after connection to the vacuum system. A built-in electric heater around the McLeod gauge is useful for this purpose.

Oil-filled McLeod gauges are possibly most useful as absolute instruments for the calibration of other gauges. They are little used in other practice.

3.5. Gauges in which the Rate of Transfer of Molecular Momentum from a Hot to a Cold Surface is Measured

In this class of gauge the pioneer contribution is due to Knudsen (K2). He considered theoretically the case where two plates were at a distance d apart in a rarefied gas and such that d was negligible relative to the dimensions of the plates, the mean free path of the gas molecules was large compared with the dimensions of the apparatus, and the accommodation coefficient at the surfaces hit by the gas molecules was unity (*see* Appendix A). If T_1 is the temperature in °K of one of the plates in the form of a fixed heater whilst T_0 is the lower temperature of the other plate in the form of a movable vane, and this vane is also at the same temperature as the surrounding walls of the gauge, then the pressure p of the gas can be shown to be given by

$$F = p/2\left(\sqrt{\frac{T_1}{T_0}} - 1\right) \tag{3.6}$$

where F is the force per unit area on the movable vane. With p in microbars, F is given in dynes per sq cm.

The outstanding feature of this result is that the force F is dependent only on the gas pressure and the temperatures and is *independent of the nature of the gas molecule*. The calibration of the gauge should therefore be the same for any gas or vapour.

Two typical forms of the **Knudsen gauge** (Fig. 3.9) are the model described by Steckelmacher (S5) and a laboratory pattern due to Lockenvitz (L5). In the latter type, the temperatures T_0 and T_1 are readily determined.

The possible range of application of this gauging principle is for pressures from 10^{-8} to 10^{-2} torr (Steckelmacher, S5). The lower limit is set by the necessity for measuring small forces F and the maximum value of T_1/T_0 which can be allowed. T_1 can hardly be set at more than about 250° C without increasing difficulties due to outgassing and also excessive radiation of heat to other parts of the gauge, whilst T_0 is conveniently at room temperature. T_0 is reduced by liquid-air cooling in some designs but this makes the gauge liable to act as a condensation sink and give pressure readings different from those prevailing in the vacuum tank. The upper limit of the pressure range is set by the mean free path of the gas molecules being reduced to the same order of size, or less than, the distance d between the plates. The calibration graph of F against p for constant T_1/T_0 then departs from the linearity, predicted by equation (3.6); in fact, the sensitivity, dF/dp, decreases and, at a certain pressure, the deflection of the movable vane is a maximum.

The Knudsen gauge thus has a range comparable with the hot-cathode ionization gauge (§ 3.9) with the advantage of a calibration independent of the nature of the gas. One would imagine, therefore, that these gauges would find

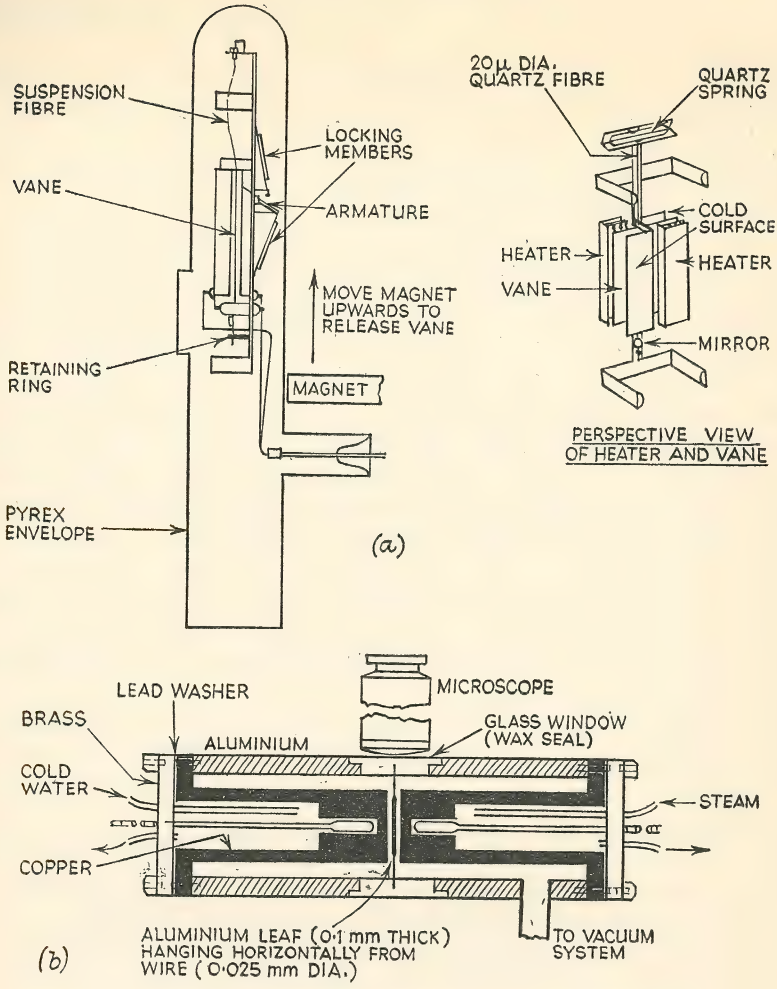


FIG. 3.9 The Knudsen gauge
(*a*) A commercial model (*after Steckelmacher*)
(*b*) The Lockenvitz gauge

widespread application. This is not the case in practice. The reasons for this may be listed as follows:

(*i*) To measure the small forces due to molecular bombardment of the moving vane, a delicate suspension is necessary. This has been overcome to some extent in more robust designs (Dumond and Pickels, DP1, and Steckelmacher, S5) but at the sacrifice of sensitivity at the lowest pressures. Experiments conducted in the authors' laboratory with a commercial glass Knudsen manometer which has been thoroughly degassed show that measurement of the pressure below 10^{-6} torr is not possible due to vibratory drifts of the vane.

To reduce the effects of mechanical disturbances on the movable vane, a permanent magnet is arranged around the gauge envelope; the motion of the vane, which is constructed, usually, of diamagnetic pure aluminium, is then nearly 'dead-beat'.

(*ii*) A precision construction of the heaters, vane and suspension is essential, with special attention to the spacing. Commercially available models are therefore expensive and the gauge cannot be readily constructed in the laboratory.

(*iii*) Models with both glass and metal envelopes have been produced. Gauges with metal envelopes cannot be properly degassed by baking, particularly because hard wax and/or Neoprene O-rings have been used in some constructions. The use of metal gauges to record pressures below 5×10^{-6} torr is, therefore, prohibited. The use of metal O-rings (§ 4.27) should, however, enable a bakeable Knudsen gauge to be constructed in stainless steel, but this has not been tried.

(*iv*) To apply equation (3.6) the temperatures of the heaters and of the movable vane must be known. Whilst it is a simple matter to determine the former (the heaters themselves may be used as resistance thermometer elements) it is not readily possible to ensure a constant and recordable vane temperature.

(*v*) Doubts have been expressed by some experimenters concerning the independence of the calibration of the nature of the gas. Fredlund (F7) considers the effect of the accommodation coefficients of the gas molecules at the surfaces at temperatures of the heaters and the vane. If this coefficient is α_1 for the heaters at temperature T_1 and α_2 for the vane at T_0, then if $\alpha_1 = \alpha_2 = 1{\cdot}0$ for one gas but $\alpha_1 = 1{\cdot}0$ and $\alpha_2 = 0{\cdot}5$ for a second gas, the gauge sensitivity for this second gas is about 50% greater than the sensitivity for the first. Leck (L3) gives a summary of experimental results of various workers for the relative sensitivity of the Knudsen gas to various gases. Steckelmacher (S5) confirms the validity of equation (3.6) at molecular pressures and assuming the accommodation coefficients of all surfaces are unity. He further claims that, provided all the surfaces involved 'have a similar finish and are not too highly polished, the effect of any accommodation coefficient is small'.

In many cases of low pressure measurements, it is only necessary to know the order of magnitude of the pressure, or that it is below a certain level. Ionization gauges of the thermal and cold-cathode types (§§ 3.9 and 3.10) are able to do this satisfactorily, despite the considerable dependence of their readings on the nature of the residual gas or vapour. The Knudsen manometer is, therefore, most frequently used when a low pressure needs to be known with greater precision, *e.g.* in research on the effects of the residual pressure on the deposition of metals *in vacuo*, and in vapour pressure determinations. Though there is some small dependence of the calibration of a Knudsen gauge on the kind of gas present, the variations of sensitivity due to this cause are certainly very much less than for ionization gauges.

With regard to the design of Knudsen gauge illustrated in Fig. 3.9(*a*) Steckelmacher (S5) gives the following details.

(1) The two heaters are in the form of indirectly-heated, thin-wall copper boxes of rectangular cross-section, containing axial, nickel–chrome heating spirals.

(2) The vane is 0·001 in. thick and made of non-ferromagnetic material, ribbed to provide rigidity. Silver or aluminium which is completely free of ferromagnetic impurities is used.

(3) The cross-section of the suspension is as small as possible to give high sensitivity. A thin strip is preferred to a cylindrical wire, phosphor-bronze being used for a gauge with a metal envelope, but silica fibres are employed in a glass gauge. Tungsten, nickel–chrome alloy and stainless steel suspensions exhibited undesirable creep during the heating of a glass envelope for degassing purposes. The silica fibre is coated with a conducting layer of vacuum-deposited metal to prevent it from acquiring an electric charge. Silica fibres of a diameter of 10 to 30 micron give suitable sensitivities.

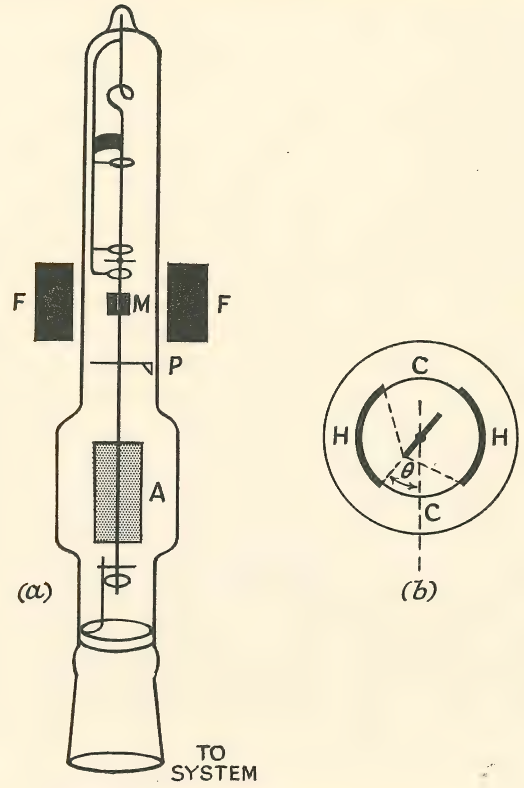


FIG. 3.10 The Gaede molvakuummeter

A commercially-available (Leybold's Nachfolger) vacuum gauge alternative to the Knudsen manometer, and one which is also suitable for measuring low gas pressures with considerable independence of the nature of the residual gas, is the **Gaede molvakuummeter** (Gaede, G4; Jaeckel, J1). Basically, this instrument consists of an aluminium vane A (Fig. 3.10(*a*)) suspended from a silica fibre (dia: 3 micron; length: 10 cm) within a cylindrical glass envelope. On the same suspension and above this vane, there is also mounted an indicator pointer P and, above this, a thin magnetized vane M; this magnet M is situated in the magnetic field provided by an external coil FF, through which an electric current may be passed. The section of the cylindrical glass wall surrounding the aluminium vane A has two externally-heated diametrically opposite surfaces HH and, between these, cold surfaces CC (Fig. 3.10(*b*)). Consider the vane A to be turned from its normal position of rest—where it lies in the diametral plane symmetrically between HH—through an angle θ. On such a rotation, the number of molecules impinging on A from the hot surfaces HH will increase whereas the corresponding number from the cold surfaces CC will decrease. The effect of these molecular impacts—which depend on the gas pressure—is to tend to restore the vane A to its symmetrical rest position. The initial rotation from the rest position is provided by passing a current through the coil F: the corresponding magnetic flux produced acts on the magnetized vane M.

Gaede (*see* Jaeckel, J1) gives two chief ways in which this instrument can be used to measure the gas pressure.

(*a*) As the vane can be made to oscillate with a period T by first deflecting it by means of a momentary current in the coil FF, a determination of T can be related to the pressure. The equation is

$$p = k\left(\frac{1}{T^2} - \frac{1}{T_0^2}\right)$$

where p is the gas pressure, k is a constant of the apparatus and T_0 is the period when the surfaces HH are at the same temperature as CC, *i.e.* the heater current supplied to HH is zero and there is, consequently, no thermal molecular force on the vane A.

(*b*) Various gas pressures (recorded by a McLeod gauge) are maintained in the molvakuummeter and the corresponding currents required in the coil F are recorded which hold the vane A at a constant deflection θ against the restoring action of the thermal molecular forces. The calibration curve—coil current against gas pressure—is largely independent of the nature of the residual gas. This is the usual method of employing the gauge.

An interesting design of a molecular manometer is also given by Klumb and Schwarz (KS2).

3.6. Thermal Conductivity Gauges

Thermal conductivity gauges of the hot-wire variety are of two chief types: (*a*) the **Pirani gauge**, (*b*) the **thermocouple gauge.** In both patterns, a filament of wire is mounted in a glass or metal envelope attached to the vacuum system, and this wire is heated by the passage of an electric current. The temperature this wire attains then depends on the rate of supply of electrical energy, the heat loss by conduction through the surrounding gas and through the support leads to the wire, and the heat loss due to radiation and convection. If the rate of supply of electrical energy is maintained constant, the temperature of the wire depends primarily on the loss of energy due to thermal conduction of the gas (where the gas pressure is low enough for convection losses to be negligible) and so on the gas pressure. In the Pirani gauge, the temperature variations with pressure are measured in terms of the change of the resistance of the wire (or dependent electrical quantity) in a Wheatstone bridge circuit. In the thermocouple gauge, a thermocouple is attached to the wire to record the temperature, and the thermo-e.m.f. is registered on a suitable galvanometer.

Von Ubisch (U1) considers analytically the loss of heat from a wire arranged along the axis of a cylindrical tube where the temperature of this wire is θ° above that of the tube wall. At molecular pressures, where intermolecular collisions are rare compared with impacts on the wire and the wall, the thermal conductivity of the gas is a function of the number of collisions with the wire and, hence, increases proportionally with the pressure. It is assumed that the wire diameter is very small compared with the tube diameter; consequently, collisions of the molecules with the wall are much more likely than with the wire so that the temperature of the gas may be put equal to the wall temperature. It may be readily calculated from kinetic theory that

$$E_K = 2\pi r_1 \alpha K_m \theta p \tag{3.7}$$

where E_K is the loss of heat from 1 cm of the wire, r_1 is the radius of the wire, α is the accommodation coefficient between the gas molecules and the wire, p is the gas pressure and K_m is the molecular conductivity of the gas given by

$$K_m = \frac{C_v + \mathbf{R}/2}{\sqrt{2\pi \mathbf{R} M T}} \tag{3.8}$$

where C_v is the specific heat of the gas at constant volume, $\mathbf{R}$ is the gas constant, M the molecular weight of the gas and T the absolute temperature of the gas.

There will also be a loss of heat from the wire due to thermal radiation. This is given by

$$E_R = 5{\cdot}67 \times 10^{-12} \, (\varepsilon_1 T_1^4 - \varepsilon_2 T^4) \tag{3.9}$$

where E_R is the radiated energy in watt/cm², ε_1 and ε_2 are the thermal emissivities of the wire and wall respectively, T_1 is the absolute temperature of the wire and $(T_1 - T) = \theta$.

As the pressure is increased above molecular values, the gas temperature in the neighbourhood of the wire increases above the wall temperature; the proportionality between pressures and heat loss due to conduction (equation 3.7) is then no longer maintained. According to Von Ubisch, this is first noticeable at pressures of 0·1 torr for wires of 0·1 mm dia, if the mean free path of the gas molecules is then significantly less than the separation between the wire and the wall. At still higher pressures, the ratio of the mean free path to the wire diameter is decisive and the wall diameter becomes unimportant. Thus, Von Ubisch records that the same dependence of heat loss (due to conduction) on pressure is obtained with 0·01 mm dia wires in capillary tubes as in tubes of 100 mm dia.

Von Ubisch refers to pressures immediately above the molecular region as *transmolecular pressures*. In this transmolecular region he gives the equations:

$$E_K = \frac{2\pi r_1 \alpha K_m \theta p}{1 + \sigma p} \tag{3.10}$$

where

$$\sigma = \frac{\alpha r_1}{k^1 \lambda} \log_e \frac{r_2}{r_c} \quad \text{and} \quad k^1 = \frac{9\gamma - 1}{\gamma + 1}$$

λ is the mean free path at the pressure p, r_2 is the tube radius, γ is the specific heat at constant pressure divided by the specific heat at constant volume, and r_c is a semi-empirical constant which is somewhat larger than r_1 at the lower pressures but equal to r_1 at the higher pressures, when $\lambda < r_1$. At these higher pressures, the motion of the molecules is limited and there is consequently a temperature difference between the surfaces (of the wall and of the wire) and the neighbouring gas layers. For high pressures, the conductivity is independent of the gas pressure and the well-known formula applies:

$$E_K = \frac{2\pi K_V \theta}{\log_e r_2/r_1}$$

where K_V is the thermal conductivity in the viscous region. In the hot-wire gauge, however, this result is modified because of the temperature discontinuities between the gas and the boundary surface. Von Ubisch gives the modified equation as:

$$E_K = \frac{2\pi K_V \theta}{\log_e (r_2 + g)/(r_1 - g)} \tag{3.11}$$

where g is a separation given to a first approximation, for the usual gases, by

$$g = \frac{15}{8} \lambda \frac{2 - \alpha}{\alpha} \tag{3.12}$$

Equation (3.11) applies, therefore, in the pressure region beyond the transmolecular one; E_K is still dependent to a small extent on λ and hence on the pressure. At still higher pressures, further phenomena occur, in particular, convection becomes important compared with conduction.

The lowest pressures recordable by hot-wire gauges will depend on the relative magnitudes of variations of the radiation loss E_R (equation 3.9) and E_K (equation 3.7). If a wire with a bright surface (*e.g.* clean tungsten) is used, ε_1 in equation (3.9) is small (about 0·3) and provided that the gauge is thermally, electrically and mechanically stable, and the wire diameter is small compared with its length, changes of pressure of 10^{-8} torr can be recorded, despite the fact that the radiation loss is of the same order of magnitude as the conduction loss at pressures of about 5×10^{-3} torr. The lower pressure limit is usually not less than 10^{-5} torr, however, and is 10^{-4} torr for commercial designs of the Pirani gauge and 10^{-3} torr for the thermocouple gauge.

Optimum sensitivity of the hot-wire gauge is considerably influenced by the choice of the temperature difference $\theta = (T_1 - T)$. This needs to be high to obtain enhanced conduction (equation 3.7) but low to reduce radiation (equation 3.9). At the higher pressures, however, the radiation loss becomes less than the conduction loss so that the temperature θ can be increased with advantage.

To obtain large values of $\theta = (T_1 - T)$ and yet restrict T_1 and, hence, radiation losses, the tube can be immersed in liquid-air. This has been done with advantage in research practice but is inconvenient in routine measurements. If T_1 is at a temperature of 120° C or more, the sensitivity, $\frac{dT_1}{dp}$, can be increased nearly ten times by reducing the wall temperature T from 20° C to the temperature of liquid-air (−187° C).

Equations (3.7), (3.8) and (3.9) indicate increased sensitivity of the gauge to the gases of smaller molecular weights. Thus, monatomic helium and diatomic hydrogen are the best heat conductors. However, von Ubisch (U1) points out that, for these two gases, the accommodation coefficients α are especially low, so that the advantage of smaller molecular weight is not as great as would appear, and, furthermore, significant effects are due to various values of C_v in equation (3.8). At higher pressures, the mean free path of the gas is important. The relative sensitivities of the hot-wire gauge for various gases will therefore be different at pressures above 0·1 torr from the values obtained at molecular pressures.

The Pirani gauge (P2) was first described by one of the authors in 1906. The practice recommended was to employ two identical hot-wire elements, one in an envelope attached to the vacuum system, in which it is required to know the pressure, and the other in a similar envelope sealed-off at the lowest possible pressure. These two elements are placed in the adjacent arms of a Wheatstone bridge, the other two arms being formed by resistors (Fig. 3.11(*a*)). This arrangement gives considerable independence from the effects of supply voltage and current variations, changes of the ambient temperature, and, furthermore, annuls the effects of changes of resistance of the elements if they become thinner with prolonged use. There are three possible methods of measurement:

(*i*) maintain the p.d. across the Pirani elements constant and observe the change in the off-balance current consequent upon a change of the wire resistance with temperature, this temperature being related to the pressure;

(*ii*) maintain the temperature—and hence the resistance—of the wire constant and measure the energy input (in terms of the supply voltage) required to do this as a function of the gas pressure;

(*iii*) maintain the current through the wire constant and measure the change of resistance as a function of the pressure.

In practice, method (*i*) is almost invariably adopted. The e.m.f. supply to the bridge is about 6 V d.c. from a car battery or from a step-down mains transformer with a bridge metal rectifier and a barretter to maintain constant current (Fig. 3.11(*b*)). Schwartz and Lavender (SL1), von Ubisch (U2) and Leck (L3) describe more complex electronic control circuits for the Pirani gauge. The bridge is balanced by variation of one of the resistance arms to give zero galvanometer deflection when the gauge attached to the vacuum system is evacuated to less than 10^{-4} torr. Higher pressures in the gauge are then subsequently measured in terms of the off-balance current recorded by the bridge galvanometer.

A development from this practice is to use Pirani filaments in all four bridge arms, two being at the pressure to be measured and two sealed-off at low pressure.

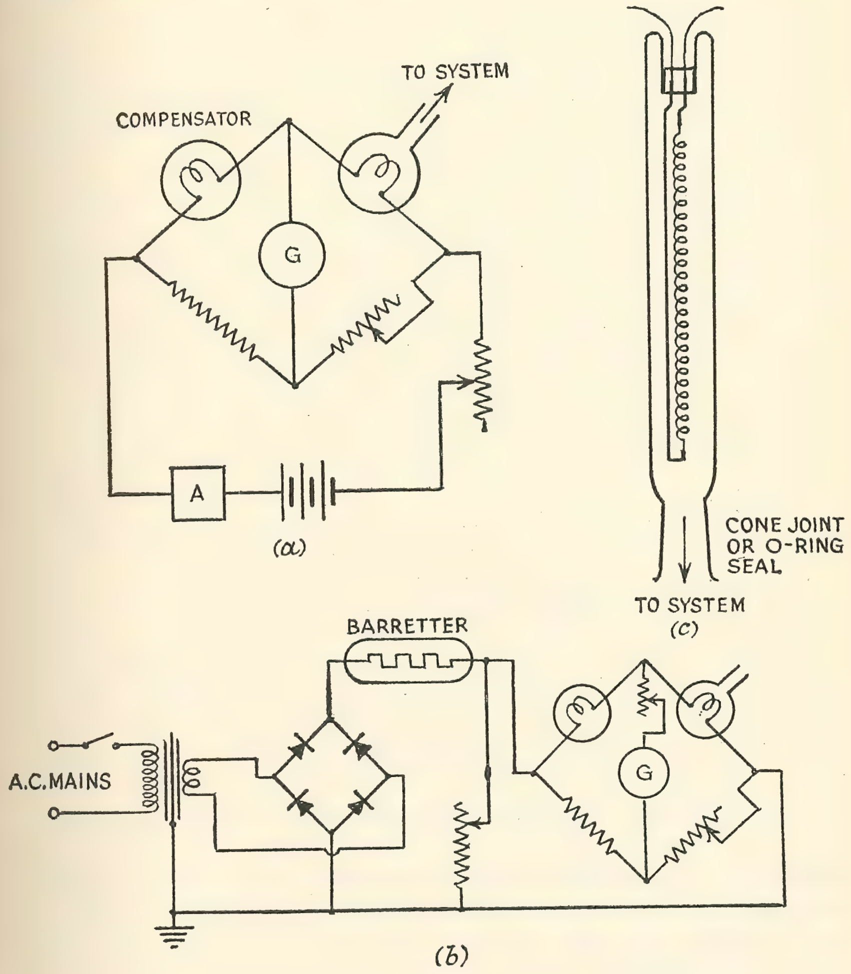


FIG. 3.11 The Pirani gauge

The Pirani filament itself is of tungsten, nickel or platinum wire 0·005 to 0·1 mm in dia and usually wound into the form of a helix of outside dia 0·5 to 2 mm and with a pitch of at least 10 wire diameters to prevent any one turn from shielding its neighbours. This filament is stretched taut between supports usually 6 to 8 cm apart to which it is spot-welded (Fig. 3.11(*c*)). An intermediate support to reduce the effects of mechanical vibration is sometimes used. The wire should have a high temperature coefficient of resistance.

The wire temperature can be increased at the higher pressures because heat loss by radiation losses is then not significant compared with loss by conduction and convection. Leck (L3) makes the following recommendations:

(*i*) for the range from 10^{-4} to 10^{-1} torr, use tungsten or platinum wire at an operating temperature of about 180° C;

(*ii*) to extend the range to 1 torr, use tungsten wire at 230° to 280° C;

(*iii*) for the range up to 5 torr, use tungsten wire at about 840° C.

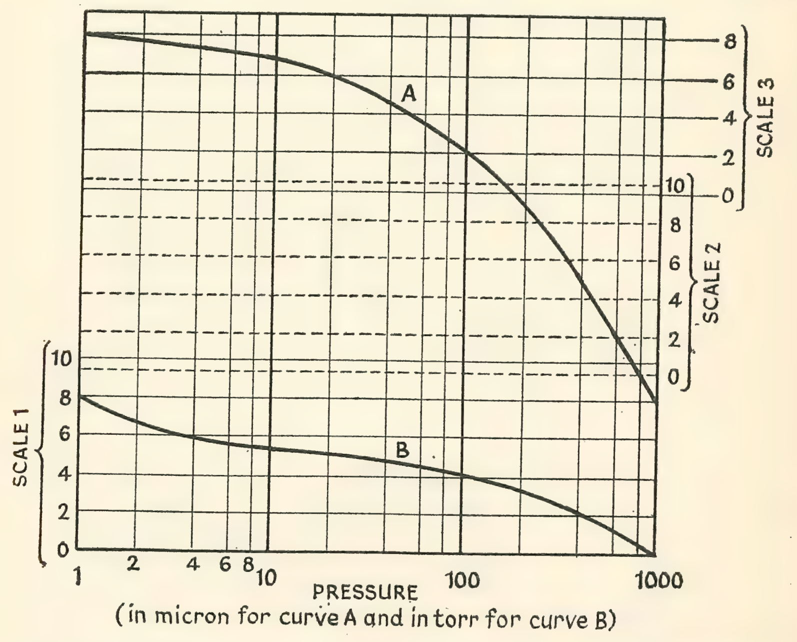


FIG. 3.12 Calibration curves for a Pirani gauge with platinum filament

Von Ubisch (U2) deprecates the use of platinum wire as it is sensitive to substances containing sulphur (*e.g.* rubber) and considers that tungsten or nickel should be used, with preference for the former. There are, however, instances of a preference for platinum despite the fact that its temperature coefficient of resistance is less than that for tungsten because it is less susceptible to oxygen and water vapour at the higher pressures. The Winston Engineering Company market a unit which employs a platinum wire, and the Westinghouse Corporation (Bloomfield, New Jersey) have developed a mobile unit for pressure measurements on lamp-making machines in which a Pirani gauge was used for pressures in the range from 10^{-3} to 760 torr. The platinum filament used was 500 mm long and 0·1 mm dia. For the lower pressures (10^{-3} to 5×10^{-1} torr) the energy dissipated in this filament was 0·4 watt and the comparison element was sealed in the bulb at low pressure whereas at the higher pressures (5×10^{-1} to 760 torr) the energy dissipation was 3 watt and the comparison bulb was at atmospheric pressure. Calibration curves for this gauge are given in Fig. 3.12. Edwards High Vacuum Ltd. market two mains-operated Pirani gauges units. One has a range from 10^{-4} to 1 torr and employs two manometer elements and two evacuated comparison elements; the other has the range from 10^{-3} to 10 torr, the comparison elements being at atmospheric pressure.

Leck (L6) points out that the rate of oxidation of tungsten increases rapidly with temperature above 600° K and that platinum, whilst it does not oxidize, suffers random changes of accommodation coefficient at less elevated temperatures. As high temperatures of about 1000° K are desirable for recording the higher pressures, Leck uses a platinum wire coated with quartz (obtained from Baker and Company, New Jersey, U.S.A.). The metal wire was 10 cm long and 0·025 mm dia and had a quartz coating approx 0·05 mm thick. The ends of the quartz coating were dissolved away with concentrated hydrofluoric acid to enable the straight wire to be soft-soldered to thick copper terminals. Excellent stability and reproducibility of readings (±2%) was obtained over the pressure range up to 6 torr with a wire temperature of 1050° K.

Leck and Martin (LM2) have more recently described a Pirani gauge for operation up to 10 torr in which the wire temperature is only 50° C. The use of a short wire gives an increased range but gives poor sensitivity. To enhance the sensitivity, therefore, a number of supports are placed along the wire to give, in effect, a number of short wires in series. Four elements, each 10 mm long, provided a range up to 3 torr; ten elements each 1·5 mm long increased the range to 10 torr.

The **thermistor gauge** (Becker, Green and Pearson, BGP1) is a Pirani-type gauge in that it employs a Wheatstone bridge circuit, but semiconductor elements with a high negative temperature coefficient of resistance are used in place of metallic filaments. On a log-log scale the calibration curve is practically linear over the pressure range from 10^{-3} to 1 torr.

The **thermocouple gauge** was first described in 1906 by Voege (V1). Dushman (D1) gives details of a number of designs. Fig. 3.13(*a*) gives the design and dimensions of a type of thermocouple gauge which can be readily constructed (Dunlap and Trump, DT1). It is interesting to note that the thermocouple gauge is more popular than the Pirani gauge on the Continent, despite the fact that its sensitivity (in watt output per unit change in pressure) is less, whereas the reverse is the case in Britain. This is probably due to concentration of effort by the manufacturers concerned on the one type of gauge rather than the other. Whereas the German firms of Leybold and Pfeiffer both market thermocouple gauges, they do not produce Pirani gauges; in Britain, on the other hand, Edward High Vacuum Ltd. market a range of Pirani gauges but do not manufacture the thermocouple gauge, though A.E.I. (Manchester, England) do so.

The Leybold thermocouple gauge is unusual in that it employs a Wheatstone bridge circuit. The gauge envelope (which can be either of glass or metal with, respectively, a cone-joint or O-ring connection to the vacuum system) contains two thermojunctions *TT* (Fig. 3.13(*b*)). These form two of the arms of a Wheatstone bridge, the other two arms being provided by the resistors *RR*. An alternating p.d. provided by a step-down mains transformer is maintained across the bridge. The alternating current passing through and heating the thermo-elements is maintained constant by the barretter B and is measured by the milliammeter mA. For a given current the temperature of the thermo-elements reaches an equilibrium determined by the thermal conductivity and hence the pressure of the surrounding gas. The thermo-elements are connected in series so that their e.m.fs are additive, as recorded by the millivoltmeter mV, which is a panel-mounted instrument directly calibrated in pressure units. A great convenience of this model is that the heating current can be regulated to various recorded values by the series-variable resistor R_1. This enables the sensitivity and pressure range of the gauge to be varied, as indicated by the graphs of Fig. 3.13(c).

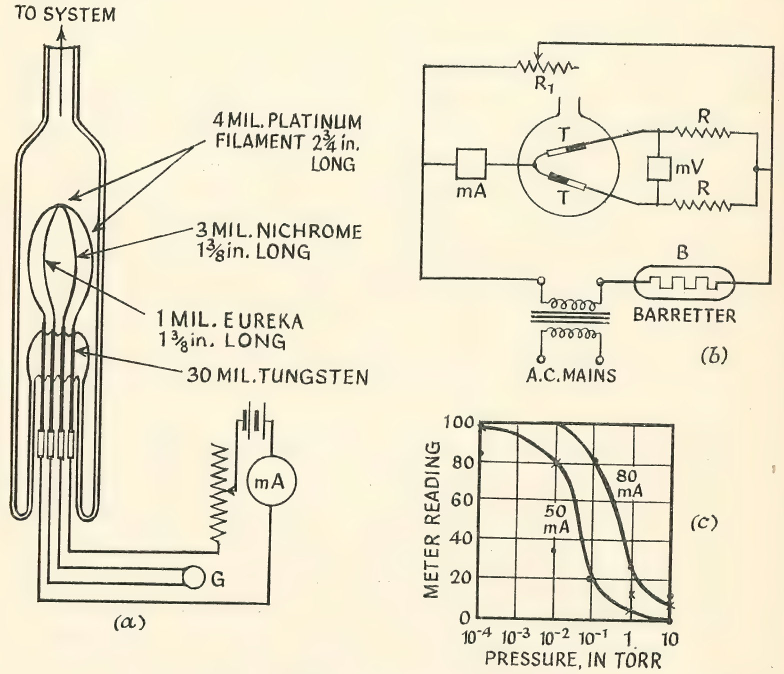


FIG. 3.13 The thermocouple gauge

Leck (L3) emphasizes the convenience of the A.E.I. design which employs a thermocouple element manufactured by Best Products Ltd. This element is only 1 cm long and requires a current of only 5 mA with a supply e.m.f. of 1 V. A 1·5 V dry cell therefore gives about two years operation. An ordinary millivoltmeter is used to record the thermo-e.m.f.

The range of the thermocouple gauge is generally from 10^{-3} to 1 torr.

The advantages of the hot-wire, thermal conductivity gauges may be listed as follows:

(*i*) The pressure is recorded with small time-lag, enabling fairly rapid variations in pressure in the system to be recorded.

(*ii*) The presence of vapours as well as permanent gases is recorded, *i.e.* the readings obtained depend on the total gas pressure and not only on the partial pressure of the permanent gas in the system, as in the case of the McLeod gauge.

(*iii*) As an output e.m.f. dependent upon the pressure is obtainable across a resistor used in place of the galvanometer in the Pirani gauge, or from the element of the thermocouple gauge, electrical apparatus such as an amplifier, a relay or an electrical recorder can be operated. Furthermore, electrically-controlled alarm systems or the operation of magnetic vacuum valves (§ 5.15) at pre-determined pressures can be arranged.

(*iv*) The electrical apparatus for the gauge, including the pressure-recording device, can be remote from the vacuum system by simply linking the gauge head to this apparatus by suitable cable. Moreover, one operating gear with appropriate switching can be used to supply several gauge heads at different points in the vacuum system, or on different systems.

(*v*) The gauges are readily adapted to leak-finding methods (Chapter 9).

Disadvantages of the gauges are:

(*i*) The calibration is dependent upon the nature of the gas; thus E_K (equations 3.7 and 3.8) is a function of the molecular weight M of the gas, the accommodation coefficient α and the specific heat C_v. No reliable and easily derived numerical relationship is possible between the galvanometer reading at a given pressure and the physical constants of the gas used. It is therefore necessary to calibrate these gauges for each gas used. Manufacturers provide, on request, calibrations for a heavier gas such as carbon dioxide as well as for air.

Though a disadvantage, this dependence on the nature of the gas can be put to good use in some circumstances. A considerable disparity between the readings of a hot-wire gauge and a McLeod gauge both attached to the same vacuum system can be used to indicate the presence of a condensable vapour, or a gas other than air, in the system (*see* for example, Le Croissette and Yarwood, LY1).

(*ii*) The gauge calibration, especially near the low pressure limit, is altered by changes in the surface of the hot wire. Possible causes of contamination of the wire surface are oxidation, sorption of gas layers and the action of back-streaming oil from an oil diffusion pump or oil vapour from a mechanical rotary pump. The sensitivity of the gauge is affected because, firstly, the contamination will alter the accommodation coefficient of the gas molecules at the hot wire and, secondly, it will affect the emissivity of the wire and hence the radiation loss. The effects of absorbed gas layers are likely to be particularly troublesome if the gauge pressure is reduced quickly from a high to a low value. A solution to this problem is to flash the gauge filament to about 900° C (red-heat) for about one minute before taking a pressure reading. On commercial instruments, this is arranged usually by the simple rotation of a switch to the 'reconditioning' position. After such flashing, the gauge should be run normally for at least one minute before a pressure reading is taken.

3.7. Variation of the Viscosity of a Gas with Pressure at Low Pressures; The Decrement Gauge

At molecular pressures, the viscosity of a gas depends on the pressure. The measurement of the variation of the viscosity of a gas with pressure can hence be utilized in designing a vacuum gauge. Various methods have been suggested (Sutherland, S6; Hogg, H7; Langmuir, L7) but the quartz-fibre manometer of Langmuir (L7) (*see also* Haber and Kerschbaum, HK2) is the simplest and perhaps the most practicable. In a design developed at the Research Laboratories of the General Electric Co. Ltd., a quartz fibre of rectangular cross-section, 0·6 × 0·15 mm, and about 60 mm long, is used. One end of this fibre is fused to form a small bead which is dipped into a suspension of carbonyl iron (Mond Nickel Co. Ltd.) in a binder of nitrocellulose (Imperial Chemical Industries Ltd. No 301/256). The coating is allowed to dry and the tip of the fibre is again dipped into the liquid. This is repeated until the iron-coated end of the fibre is attracted to a small magnet placed about $\frac{1}{4}$ in. away. The other end of the fibre is then sealed via a graded glass seal (G.E.C. WQ31) to a tungsten rod. This rod, which is beaded over the middle 10 mm with G.E.C. W1 glass, is then sealed into a W1 glass tube of 12 mm dia so that the fibre hangs vertically. The glass tube is then joined to the vacuum system concerned.

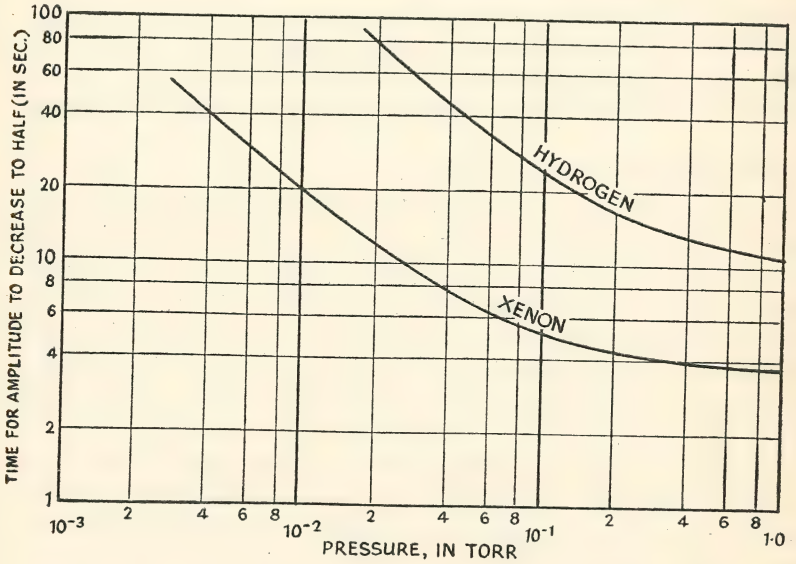


FIG. 3.14 Calibration curves for a viscosity gauge (*Courtesy of General Electric Co. Ltd.*)

The vertical fibre is illuminated from one side and viewed through a telescope furnished with an eye-piece scale. The fibre is set vibrating by drawing the small mass of iron at the lower end to the side wall of the gauge by means of an external magnet. To calibrate the gauge, the time taken for the amplitude of vibration to decrease to half of its initial value is plotted on log-log paper against the pressure (Fig. 3.14). The useful range of the gauge is from 10^{-4} to 1 torr, though some scatter of readings is obtained at pressures below 10^{-2} torr, a phenomenon possibly due to the abrupt change of cross-section at the joint between the fibre and the support.

Theoretical study of the viscosity gauge leads to the equation:

$$p\sqrt{M} = \frac{A}{t} - B \qquad (3.13)$$

where p is the gas pressure, M the molecular weight of the gas, t the time taken for the amplitude of vibration to decrease by half and A and B are constants characteristic of the fibre used.

The low pressure limit is set by the large values of t involved. As M increases, t is less for a given pressure. The operation of the gauge at low pressures improves, therefore, with the gases of higher molecular weight, in contrast to the case of the thermal conductivity gauges, a fact which sometimes leads to a preference for the viscosity gauge.

The viscosity gauge is inconvenient because optical observation over a period of several seconds is necessary in taking low pressure readings. It is chiefly used in recording the pressures of corrosive gases and vapours such as bromine, chlorine and ammonia, which would contaminate seriously the metal parts of other gauges. Even in this case, however, the Pirani gauge with a wire protected by a quartz sheath is an alternative.

3.8. Indicator Gauges Employing a Gaseous Discharge

The appearance of the glow discharge in a discharge tube can be used to give the order of pressure in a vacuum system over the range from about 10^{-2} torr to 10 torr (Yarwood, Y3). A practical form of shielded discharge tube is marketed by A.E.I. (Manchester) Ltd. (Fig. 3.15).

To improve the correlation between the observation of the nature of the glow discharge and the pressure, two main techniques have been adopted. The first is to measure the applied p.d. (in terms of the length of the spark between polished metal spheres of a given size) across the discharge tube at which the discharge disappears. The second is to include a fluorescent screen in the discharge tube. This second procedure is used in the **skanascope**, made by the Skaneateles Manufacturing Company. In this instrument, the electrodes are a cylindrical metal tube around an axial metal rod. A discharge is initiated at a certain pressure p_i by means of a given peak alternating p.d. between the rod and cylinder. As the pressure is reduced, the current in the discharge decreases and then drops abruptly to almost zero at a certain pressure p_f. The discharge excites a fluorescent screen inserted in one end of the metal cylinder. The intensity of the luminescence of this screen serves as a vacuum indicator. For air, the range of pressures from p_i to p_f is about 6×10^{-1} to 3×10^{-2} torr, but extension down to 5×10^{-3} torr is possible in improved designs. The indications depend on the nature of the gas present.

A semi-quantitative vacuum tester has been suggested by Pirani (Pirani

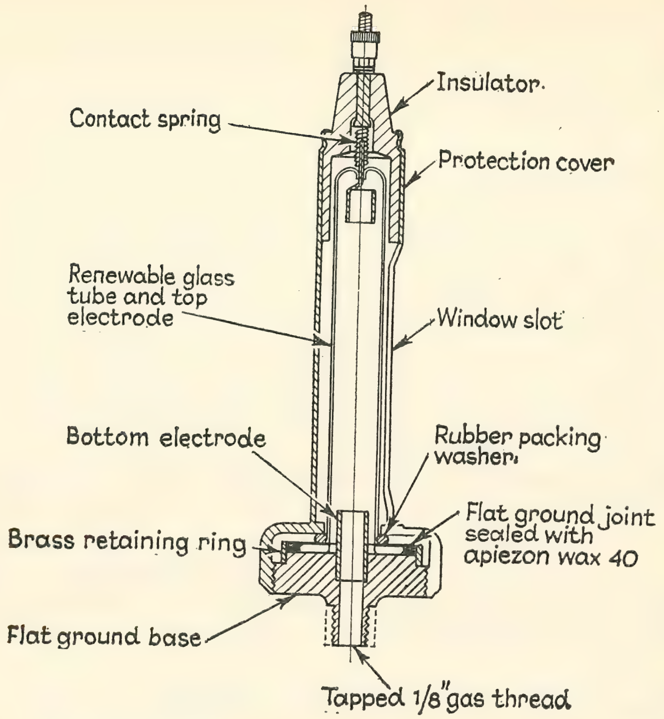

Insulator
Contact spring
Protection cover
Renewable glass tube and top electrode
Window slot
Bottom electrode
Rubber packing washer
Flat ground joint sealed with apiezon wax 40
Brass retaining ring
Flat ground base
Tapped 1/8" gas thread

FIG. 3.15 The discharge tube (*A.E.I. (Manchester) Ltd.*)

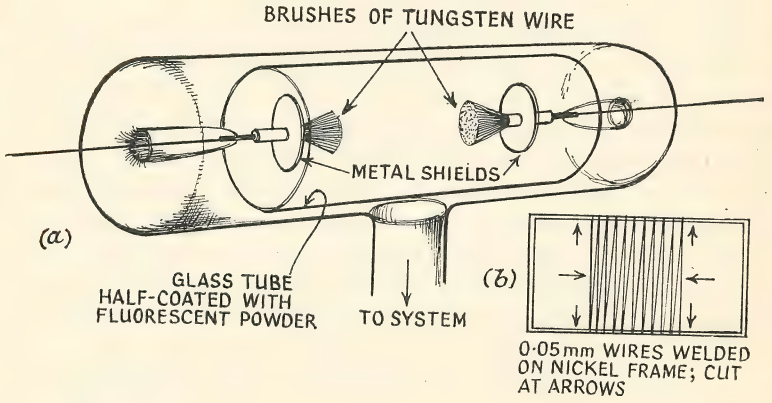

BRUSHES OF TUNGSTEN WIRE
METAL SHIELDS
(a)
GLASS TUBE HALF-COATED WITH FLUORESCENT POWDER
TO SYSTEM
(b)
0·05 mm WIRES WELDED ON NICKEL FRAME; CUT AT ARROWS

FIG. 3.16 A semi-quantitative vacuum indicator

and Neumann, PN1) in which a glass cylinder of about 1½ in. dia and 6 in. long is fitted with a tungsten wire brush electrode at each end (Fig. 3.16(*a*)). These brushes consist of 0·05 mm dia wires opened at one end and welded to the sealed-in lead wire at the other. A method of construction for such a brush is illustrated in Fig. 3.16(*b*). Immediately within the main envelope tube is situated an inner coaxial cylindrical glass tube almost as large as the envelope half-coated with fluorescent powder (zinc silicate activated with manganese). A convenient source of supply across the brush-shaped electrodes is a 'Tesvac' (a Tesla type coil supplied by Ferranti Ltd. which provides 30 kV off-load and a maximum current of about 1 mA). At gas pressures above 10^{-2} torr, this indicator behaves like a normal discharge tube. Below 10^{-2} torr (where the usual discharge tube would begin to 'black out') scintillations appear at the fluorescent screen owing to the impact of electrons arising on field emission from the fine-pointed wires of the brush electrodes. The inner cylindrical tube within the main envelope is essential because there is the danger that the electrons might pierce the tube walls. The fluorescence is a maximum at about 10^{-3} torr and becomes weaker and weaker down to about 10^{-5} torr, but does not fade out. At the same time, the p.d. across the tube rises steeply to a maximum, which can be registered by an adjustable spark-gap connected in parallel.

Though such a device cannot be calibrated precisely, yet it is often adequate in vacuum practice to know only the order of pressure prevailing, or that it is below a certain value. Such a simple indicator is therefore often as useful as a more complex vacuum gauge like the Penning gauge in industrial practice.

3.9. Measurement of an Ionization Current Produced in the Residual Gas; The Hot-cathode Ionization Gauge

The hot-cathode ionization gauge is based on a three-electrode tube (or a tetrode, in some designs) in which a thermionic cathode emits electrons, these electrons are accelerated to a positive electrode (usually a grid) and the positive ions produced by collisions of the electrons with the residual gas molecules are collected at a negative electrode (the ion collector). The positive ion current recorded is dependent upon the gas pressure prevailing in the gauge. The first designs were developed independently by Buckley (B4) in America and by Hausser-Ganswindt and Rukop (HR2) in Germany.

The thermionic cathode is usually of the directly-heated filamentary type and may be of tungsten, thoriated tungsten or an oxide-coated wire. The positive electrode is usually a cylindrical grid around the filament and maintained at a potential with respect to the filament of V_g, where V_g is 100 to 200 V, *i.e.* well above the ionization potentials of the gaseous elements (*see* Table A1, p. 516). The negative electrode—ion collector—is then a surrounding coaxial cylindrical electrode (the anode of a triode valve) in the conventional construction, and it is maintained at a potential with respect to the filament of V_c, where V_c is usually between -10 and -25 V.

This design is illustrated by the Mazda 29D2 ionization gauge head (Fig. 3.17(*a*)). The rôle of the grid and the anode can be reversed, *i.e.* the grid can be held negative and act as the positive ion collector whilst the outer anode is positive. However, the operation is then less stable and the gauge has only about half the sensitivity to pressure variations. Fig. 3.17(*b*) shows a very simple design consisting of three identical filaments which can be used as the appropriate electrodes; this design is very easily degassed and is able to record pressures down to 10^{-6} torr. Fig. 3.17(*c*) illustrates a design due to Morse and Bowie; the grid is again a spiral of tungsten wire which can be degassed by the direct passage of an electric current, whilst the ion collector is in the form of a platinum film on the inside of the Pyrex glass wall, which can be degassed by heating with a blow-pipe flame.

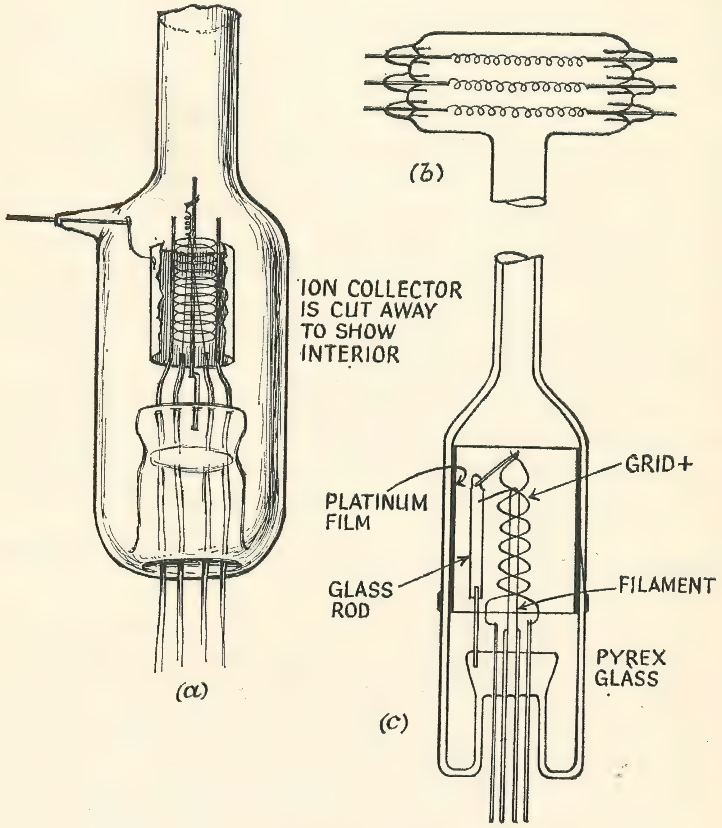


FIG. 3.17 Hot-cathode ionization gauges

With the grid positive to collect electrons and the outer plate negative, the electrons leaving the filament will make a number of excursions to and fro through the grid wires before collection at this grid. If the ion collector is more than 5 V negative, the electrons will not reach its surface but be turned back immediately outside it. The region of gas ionized by the electrons is therefore the annular space between the grid and the ion collector (anode in the usual triode valve). The number of positive ions produced per electron per cm of path at a pressure of 1 torr (the pressure usually quoted, though it is much higher than is usual in the ionization gauge) is a measure of the efficiency of the ionizing process. This efficiency is a maximum for electron energies of 100 eV approx. In the conventional hot-cathode ionization gauge, therefore, the grid voltage is usually at 150 V to 200 V to ensure that as high a proportion as possible of the electron collisions with gas molecules occur at near maximum efficiency. The basic circuit is shown in Fig. 3.18.

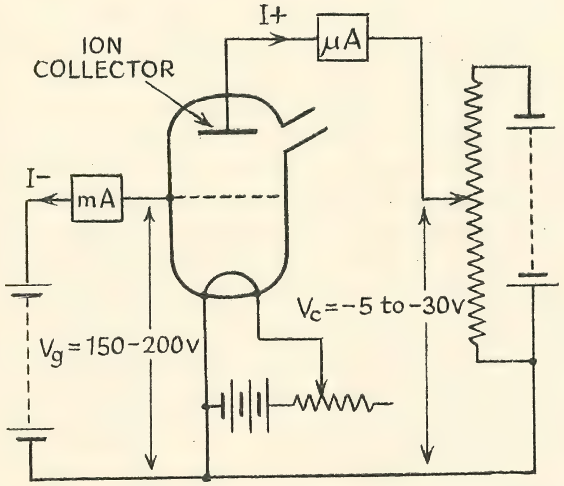


FIG. 3.18 Basic operating circuit for a hot-cathode ionization gauge

If the electron current to the grid, I_-, is kept constant and V_g and V_c are also constant, the positive ion current, I_+, is directly proportional to the gas pressure, provided that the mean free path of the gas molecules is not less than the grid-ion collector clearance and, furthermore, I_+ is not more than 0·1 I_-. In practice, this linearity of calibration is maintained up to pressures of about 10^{-3} torr. Furthermore, I_+ is directly proportional in these circumstances to I_-. Consequently,

$$I_+ = SpI_-$$

or

$$S = \frac{I_+}{pI_-} \tag{3.14}$$

where S is the sensitivity of the gauge. S is usually quoted with the positive ion current I_+ in microamp, at a pressure of one micron, and for an electron current I_- of 1 mA, *i.e.* S is given in μA/μ/mA. In specifying S for a particular gauge, V_g and V_c must be stated and also the nature of the gas concerned. For example, the Mazda 29D2 gauge has a sensitivity for air of 20μA/μ/mA with $V_g = 200$ V and $V_c = -20$ V.

S will depend not only on the electrode arrangement and the electrode potentials but also on the gas concerned. As the electron paths in the gauge are complex and there is, furthermore, no simple relationship between the ionization efficiency and the electron energy, it is not possible to derive practicable formulae for the calculation of S (*see* Leck, L3, for an account of the theory) and it is hence necessary to calibrate the gauge against the McLeod gauge. Leck (L3) gives tabulated data on the relative sensitivities of the hot-cathode ionization gauge for various gases. These figures have a variation of only ±20% for a given gas at given operating potentials from one type of triode gauge to another. Referring to nitrogen as unity, figures for other gases range from 0·16 approx for helium to 3 approx for mercury.

Kinsella (K3) has discussed the effect of the electrode geometry on the sensitivity of the conventional design of hot-cathode ionization gauge. He considers that it is necessary to increase the path of the electrons with energies above the ionization energy before they are collected by the positive electrode. This consideration has also influenced earlier designs of gauge in which the electrons were made to execute spiral and oscillatory paths by the use of a superimposed magnetic field (Makinson and Treacy, MT1). There are two possibilities of increasing the electron path in a simple design with a V-shaped filament surrounded by a coaxial cylindrical grid and an outer, coaxial ion collector: (*a*) use a larger grid-to-ion collector clearance; (*b*) decrease the grid wire diameter and increase the pitch. The latter would increase the electron paths because, with reduced grid area, the electrons would oscillate more about the grid before collection. Electrostatic field configurations forbid extension of these two factors beyond certain limits. An optimum design with a sensitivity of 30μA/μ/mA is given as:

filament: V-shaped; dimensions relatively unimportant; 0·2 dia wire, 4 cm total length;

grid: helix of 1 cm dia with optimum pitch of 4 mm; grid wire of dia 0·2 mm; gives sensitivity with freedom from Barkhauszen–Kurz oscillations;

ion collector: cylinder of height 3·5 cm and dia 4 cm.

The range of pressures over which the ionization gauge is usable is from 10^{-8} torr to 10^{-3} torr for the conventional design. Departure from linearity of the I_+ against p curve occurs above 10^{-3} torr, as already mentioned, but the real factor limiting the use of this gauge at higher pressures is the action of gases on the hot cathode. The filament of tungsten or thoriated tungsten has a life decided primarily by oxygen attack, whilst oxide-coated cathodes are readily poisoned by small traces of oxygen or water vapour.

The low pressure limit is set by the release of electrons from the ion collector due to the photoelectric action of X-rays and also of light from the filament. The action of the X-rays is the more important phenomenon. These X-rays are produced at the grid by the electrons which arrive there with energies of about 150 eV. A fraction of the X-rays produced are intercepted by the ion collector. The consequent loss of electrons released from the ion collector results in a current, I_x, which cannot be distinguished by the measuring instrument from the current I_+ due to arriving positive ions (Nottingham, N1). I_x is a constant depending on V_g, I_-, the geometry of the electrodes and the nature of the grid surface, but is *independent of the pressure*. For a conventional pattern of ionization gauge, I_x is the same order of size as the positive ion current I_+ at a pressure of about 10^{-8} torr. At such pressures, therefore, the ion collector current becomes constant irrespective of the pressure.

In the **ultra high vacuum ionization gauge** (Bayard and Alpert, BA1) the low pressure range is extended down to 10^{-10} torr, or even lower, by ensuring that the ion collector intercepts only 1% or less of the X-rays produced at the positive grid. To arrange this, the thermionic filaments are erected outside the grid whilst the ion collector is a thin, axial wire. The ion collector current, I_c, against pressure curve has been shown to be linear down to these very low pressures. Fig. 3.19(*a*) illustrates a design (Yarwood, Y4) based on the original Bayard–Alpert pattern, Fig. 3.19(*b*) shows a recent Alpert model. Amongst developments from the Bayard–Alpert pattern, those due to Nottingham (N2) and Metson (M3) are noteworthy. The Nottingham gauge has flat spiral grid structures across the ends of the cylindrical electron collector to ensure enclosure of the ionization region, and a cylindrical screen-grid is arranged outside the normal electron collector grid. This screen-grid is maintained at a large negative potential to increase the average path of the

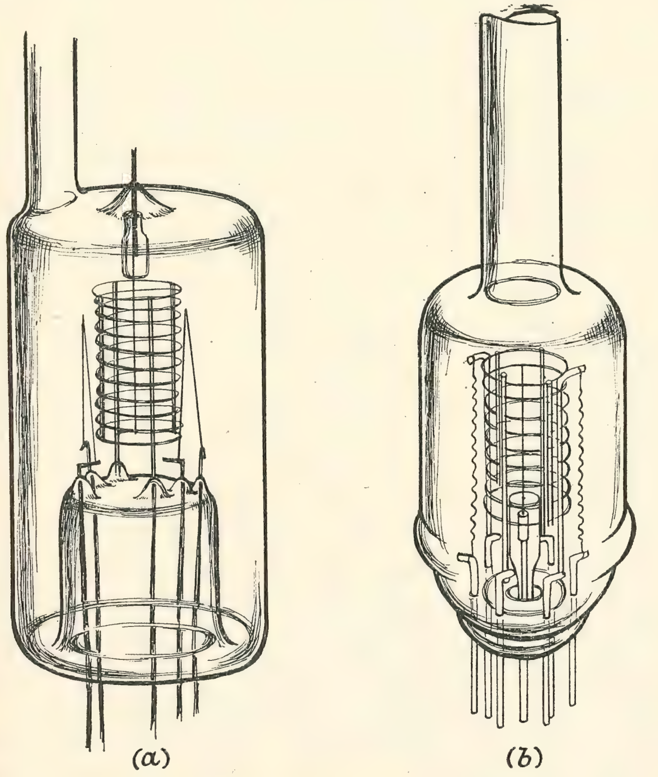


FIG. 3.19 Ultra-high vacuum ionization gauges of the Bayard–Alpert design

electrons in the ionization region and also to act as a shield against the effects of wall charges. The Metson gauge reduces the effects of X-rays to a very low order by the use of a suppressor shield.

The sensitivity S of the Bayard–Alpert gauge is comparable with that of the conventional pattern because the electrons within the ionization region inside the cylindrical grid will have been accelerated to the full grid potential V_g.

Circuits for hot-cathode ionization gauges. The basic operating circuit is shown in Fig. 3.18. Choosing a figure of 20μA/μ/mA as a usual sensitivity, it is readily seen that the microammeter in the ion collector circuit must be able to record a current of $\frac{20 \times 10^{-7}}{10^{-3}}$, *i.e.* 2×10^{-3} μA, if pressures of 10^{-7} torr are to be registered. On this basis, Table 3.3 is constructed showing the lowest pressures recordable with a maximum error of ±10% (on the basis of a scale reading of 1 cm readable to ±1 mm) where commercially available microammeters of the lamp-and-scale pattern with various sensitivities and a period of about 2 sec are used.

TABLE 3.3

Galvanometer current sensitivity, mm/μA	Resistance of galvanometer, ohm	Lowest pressure recordable where $S = 20$ μA/μ/mA torr
120	20	$4{\cdot}2 \times 10^{-6}$
200	50	$2{\cdot}5 \times 10^{-6}$
1100	450	$4{\cdot}5 \times 10^{-7}$

It is seen that to record pressures below 5×10^{-7} torr it is necessary to use a d.c. amplifier to amplify the ion current. In practice, it is preferable to do this for pressures below 10^{-6} torr to obtain the convenience of a panel-mounted, moving-coil instrument instead of the sensitive lamp-and-scale galvanometers which demand a mirror-scale distance of 1 metre.

A suitable d.c. amplifier which utilizes a twin-triode valve in a cathode-follower circuit is shown in Fig. 3.20. The necessary power-pack with voltage regulator tubes is also included.

By means of electrometer valves in balanced circuits (Yarwood and Le Croissette, YL1) or, preferably, a vibrating reed electrometer (Palevsky, Swank and Grenchik, PSG1) it is possible to record accurately currents of 10^{-14} amp and to indicate 10^{-15} amp. Such sensitivities enable a pressure reading of 5×10^{-13} torr to be recorded, assuming the ionization gauge sensitivity to be 20μA/μ/mA. This is well below the X-ray limit of the conventional gauge and is quite adequate even for the Bayard–Alpert ultra-high vacuum gauge. Indeed, a Bayard–Alpert gauge head with a vibrating reed electrometer to amplify the ion collector current forms a very useful arrangement for recording the very low pressures from 10^{-8} to 10^{-11} torr.

To ensure stable operation of a hot-cathode ionization gauge it is essential to maintain constant the electrode potentials and the electron current I_- to

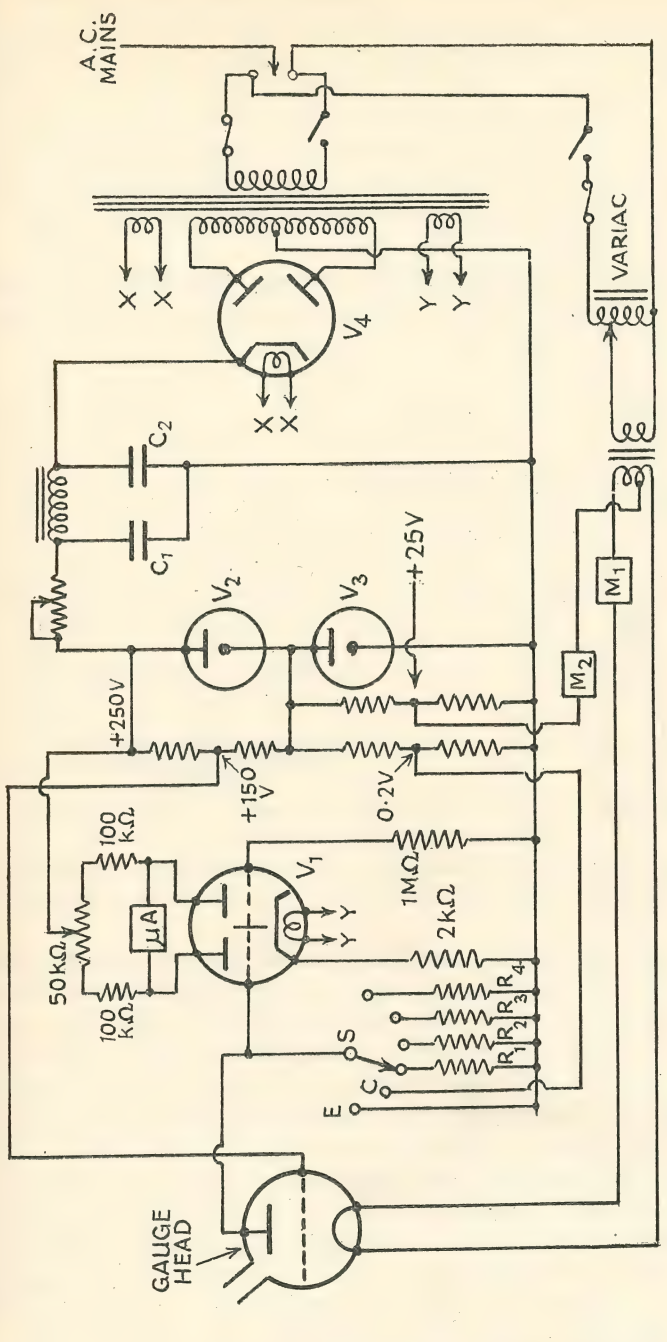


FIG. 3.20 A convenient operating circuit for a hot-cathode ionization gauge with d.c. amplifier and stabilized power supply

the positive grid. The use of voltage regulator tubes is adequate to preserve constant values of V_g and V_c, but it is more difficult to ensure constant values of I_-. In a manually controlled circuit, the gauge filament voltage can be supplied from a step-down transformer of which the primary voltage is regulated by a Variac. The use of a milliammeter in the grid circuit then enables I_- to be adjusted to 1 mA, 5 mA, or 10 mA, as the case may be, and any alterations of I_- can be compensated by adjustment of the filament current. This practice is often used, but it is inconvenient in industrial application and, particularly, where a recorder is to be run from the gauge which is to receive the minimum of attention.

Electronic control circuits to stabilize the emission from a thermionic cathode. These are mostly based (Leck, L3) on the original circuit due to Ridenour and Lampson (RL1) (Fig. 3.21).

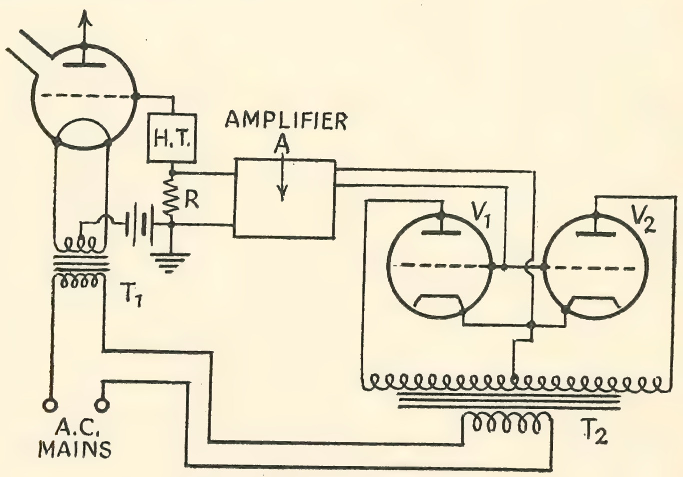


FIG. 3.21 The basic circuit of Ridenour and Lampson for the stabilization of the emission from a thermionic filament in a hot-cathode ionization gauge

In this circuit, the valves V_1 and V_2 act as loads on the secondary of the transformer T_2: any variation of the resistances of these valves is reflected back into the primary of T_2. The primary of T_2 is in series with that of transformer T_1, where the secondary of T_1 supplies the filament voltage of the ionization gauge head. If the electron current, I_-, to the grid of the gauge head alters because of a change in the emission from the gauge filament, a corresponding signal voltage is produced across the resistor R in series with the h.t. supply to the gauge grid. This signal voltage is fed to the amplifier A and then to the input of the valves V_1 and V_2. It is readily arranged that an increase of the current I_- causes an increase of the negative voltage on the grids of V_1 and V_2 (and vice versa). As the resistance of V_1 and V_2 across the secondary of T_2 increases, so does the reflected load in the primary of T_2, and hence the gauge filament current decreases. An increase of I_- (or a decrease) is, therefore, offset by a decrease of the filament emission (or an increase).

This circuit therefore provides stabilization against changes of the supply voltage and of the emission of the gauge filament due to variations of its current, work function or resistance.

King (K4) gives full details, with component values, of a control unit based on the Ridenour and Lampson circuit but which is stated to have greater simplicity.

Steckelmacher and Van der Meer (SV1) assert that the Ridenour and Lampson circuit has the inherent disadvantage of narrow stabilization range due to the magnetizing current of T_2, which determines the lowest gauge filament current attainable. Though this circuit was able to maintain I_- constant at 10 mA despite filament current changes from 1·4 to 2 amp, it is stated that a wider variation from 0·5 to 2·5 amp may be expected in the life of an ionization gauge with an oxide-coated cathode. To achieve this wider range of stabilization, these workers developed the circuit illustrated basically by Fig. 3.22(*a*), whilst Fig. 3.22(*b*) shows the complete arrangement with recommended component values.

Referring to Fig. 3.22(*a*), it is seen that the primary of the gauge filament transformer T_1 is divided into two sections A and B which are loads in the anode circuits of the valves V_1 and V_2, respectively. Each of these valves passes half-a-cycle, respectively, of the current from the centre-tapped secondary of the mains transformer T_2. The gauge electron current I_- produces voltage across the resistor R. This signal voltage is made the input to the pre-amplifier, the output of which is fed to the grid-cathode input of valves V_1 and V_2. An increase in electron current I_- is arranged to provide an increase of the negative bias on V_1 and V_2 and, consequently, a decrease of the voltage across the gauge filament, and vice-versa.

The use of a space-charge grid maintained slightly negative between the cathode and the positive grid of a hot-cathode ionization gauge gives a tetrode design of gauge head in which the electron current I_- can be controlled and stabilized readily. The circuit of Bouwmeester and Warmoltz (BW1) is described by Leck (L3).

The outstanding advantage of the hot-cathode ionization gauge is its ability to record very low pressures; it is, indeed, the only vacuum gauge able to record satisfactorily pressures below 10^{-7} torr. It also has the advantages of an electrically controlled instrument in that recording can be remote from the gauge head.

The disadvantages of this gauge restrict its use to the pressure range below 10^{-3} torr and lead to the necessity for careful setting-up and use of the gauge and its associated circuit if reliable pressure readings are to be obtained. Even so, considerable errors may result.

Difficulties attendant upon the use of this gauge, assuming that the emission is stabilized, are:

(1) The calibration is markedly dependent on the nature of the gas. Calibration is usually against a McLeod gauge and linearity of the collector current against pressure is assumed down to the lowest pressures of 10^{-10} torr if a

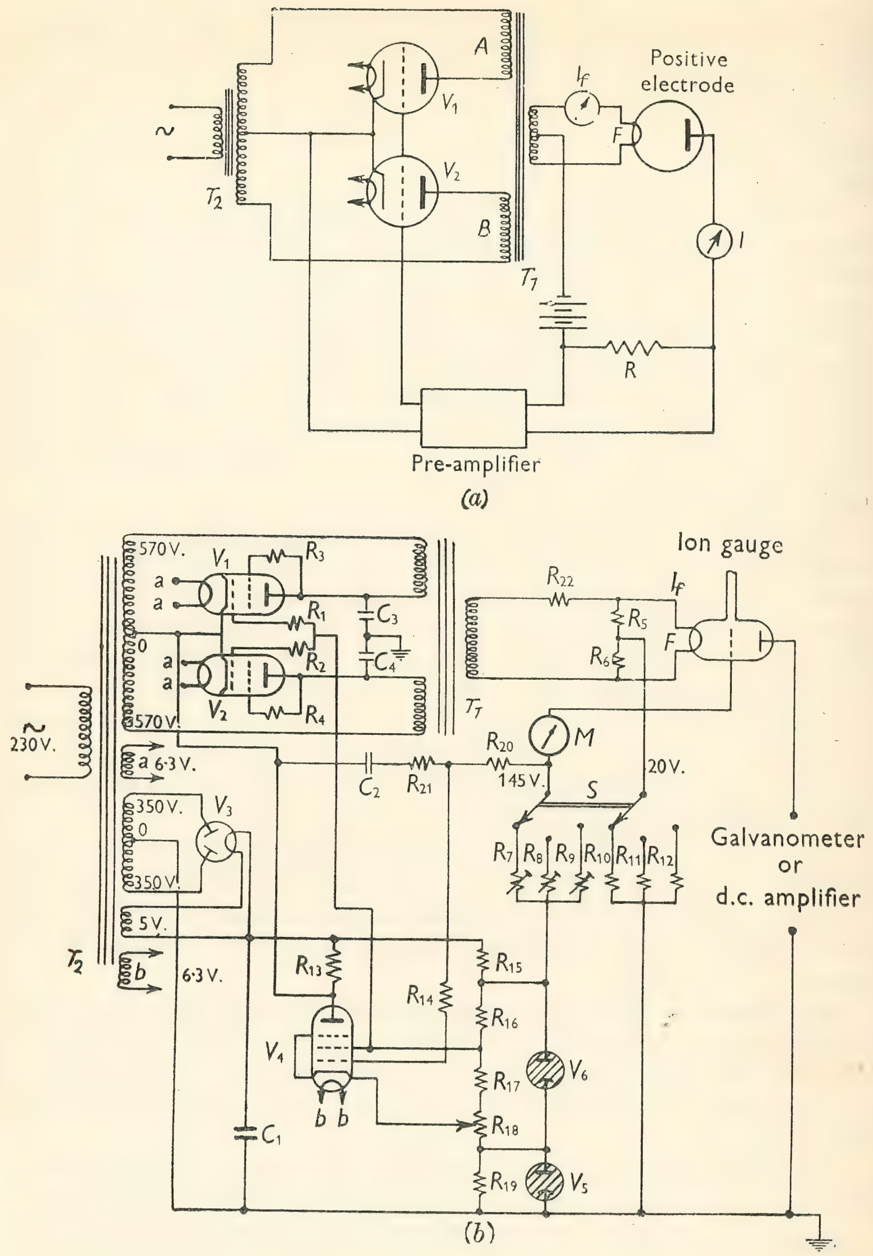


FIG. 3.22 Automatic emission regulator for an ionization gauge (*Steckelmacher and van der Meer*)

$R_1 = R_2 = 10$ kΩ; $R_3 = R_4 = 100$ Ω; $R_5 = R_6 = 56$ Ω; $R_7 = 150$ kΩ; $R_8 = 30$ kΩ; $R_9 = 7{\cdot}5$ kΩ; $R_{10} = 20$ kΩ; $R_{11} = 4$ kΩ; $R_{12} = 1$ kΩ; $R_{13} = 470$ kΩ; $R_{14} = 2{\cdot}2$ MΩ; $R_{15} = 2$ kΩ; $R_{16} = 5{\cdot}6$ kΩ; $R_{17} = 2{\cdot}8$ kΩ; $R_{18} = 4$ kΩ; $R_{19} = 10$ kΩ; $R_{20} = 1$ MΩ; $R_{21} = 1{\cdot}5$ MΩ; R_{22} to suit maximum safe filament current. $C_1 = 8$ μF.; $C_2 = 0{\cdot}1$ μF.; $C_3 = C_4 = 0{\cdot}001$ μF. $V_1 = V_2 =$ KT66; $V_3 =$ 5U4G; $V_4 =$ EF36; $V_5 = V_6 =$ S130. T_1, transformer with two primary windings 300 V each, secondary 10 V

Bayard–Alpert type head is used. Leck (L3) points out that the relative sensitivities to various gases for various gauge heads with the same electron accelerating voltage V_g agree to within ±20 % and, therefore, tabulated values of these sensitivities (given by Leck) can be referred to in using the gauge for various gases. However, at low pressures near the ultimate of a diffusion pump, the nature and partial pressures of the constituent gases is generally not known.

(2) The gauge acts as a pump due to (*a*) sorption of gas at the hot cathode, especially of oxygen and atomic hydrogen (which is formed from molecular hydrogen in the gauge) and (*b*) due to sorption of gas conveyed to the ion collector (and the glass walls) in the form of positive ions (*see* § 7.3 for an account of ion pumping). In view of this, and also because of outgassing of the gauge, Blears (B5) emphasizes that a 'high-speed' ionization gauge is necessary if serious errors are to be avoided. This means that the gauge should either be connected to the system by short, wide tubing of low impedance to gas flow, or, preferably, the gauge electrodes should be erected in the test dome on the pump head. Otherwise, the sorption (or evolution) of gas by the gauge will result in considerable pressure differences across tubulation of significant impedance. The **high-speed ionization gauge** is particularly necessary in measuring low pressures produced by oil diffusion pumps because of the uncertain way in which hydrocarbons from the oil will react with the hot gauge. Both Hickman and Blears assert that two ionization gauges, one degassed and the other undegassed, connected to an oil diffusion pump will ultimately record the same pressure, but, whereas this pressure is only recorded after several hours if the gauge tubulation has a conductance of, for example, 0·7 litre per sec, it is registered after only about 5 min if this conductance is 80 litre per sec. This difference will be particularly aggravated if the ultimate of the oil diffusion pump is attained because the diffusion pump speed will then be zero whereas the ionization gauge will still have significant pumping speed.

The suggested arrangement of Blears of an ionization gauge in a test-dome on a diffusion pump is shown in Fig. 3.23.

Ionization gauges of the high-speed type with wide-bore connecting tubulation are now a standard manufacturers' item.

(3) In recording low pressures below 10^{-6} torr, outgassing of the gauge is significant. The gauge must therefore be degassed thoroughly before use, and every time after the pressure in it has been allowed to rise above about 10^{-2} torr. Degassing requires, firstly, baking in an oven to about 400° C, secondly, elevation of the temperature of the electrode structure of the gauge to 800 to 1000° C. Degassing of the electrodes can be accomplished by eddy-current heating, by electron bombardment, or by direct passage of current through the filament and grid of a suitably designed gauge head. Eddy-current heating demands the use of expensive auxiliary equipment and is, furthermore, not readily possible with gauges of the Bayard–Alpert construction. To arrange electron bombardment, the filament is over-heated (usually with 1½ times the normal filament current) and the grid and ion collector are strapped

together and raised to a positive potential so that an electron current of 50 mA to 100 mA or more is drawn to these electrodes. This requires special provision in the power-pack used for the gauge supply voltages. A convenient practice is to take the necessary potential directly from the smoothing capacitors of the power-pack, a suitable switch, regulator and milliammeter being set up in a 'degassing circuit'.

However, electron bombardment is deprecated by some workers because it is very likely to damage the gauge filament, especially when hydrocarbons (*e.g.* from pump oil) are present in the gauge envelope. An alternative practice which is more easily arranged is therefore adopted, by, for example, Vacuum Industrial Applications Ltd., and the National Research Corporation. Their gauges (model 507) have a grid in the form of a tungsten spiral through which an electric current can be passed (directly to the gauge head pins from a suitable mains step-down transformer) to raise the temperature gradually to 800° C. The heat from this grid heats the cylindrical ion collector by radiation. The filament is not switched on before a vacuum of 10^{-3} torr is produced and is never over-run. However, experience over a long period with this type of gauge head to record pressures down to 10^{-8} torr indicates that it is occasionally necessary to heat the ion collector to a higher degassing temperature than can be achieved by radiation from the heated grid.

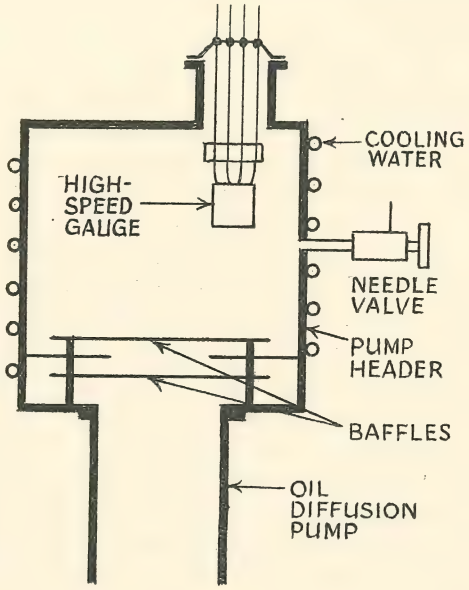
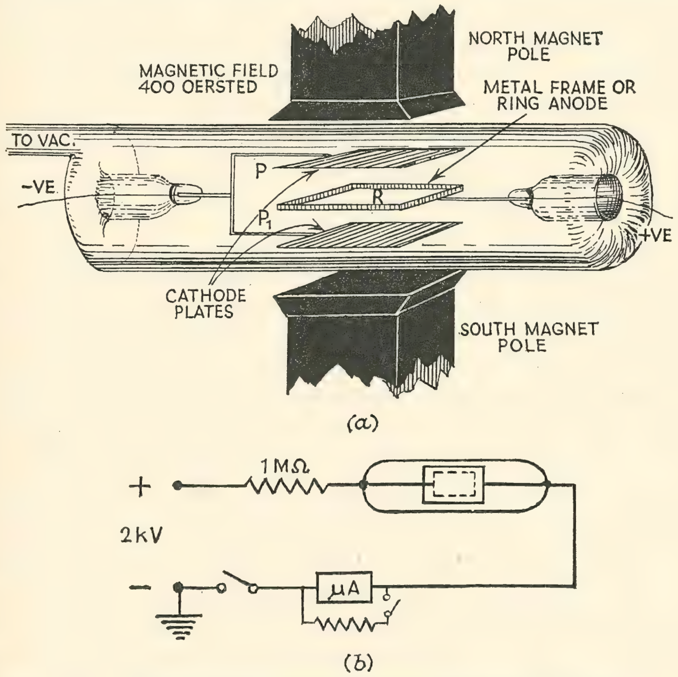


FIG. 3.23 The use of a high-speed gauge to record the ultimate pressure of an oil diffusion pump (*after Blears*)

(4) It is not uncommon to find that dissatisfaction is expressed concerning hot-cathode ionization gauges because of the short life of the filament. Unduly short life is often due to inadequate attention to correct use and to undue application of the electron bombardment technique for degassing. If a system is used in which the pressure in the gauge is likely to increase above 10^{-3} torr, a safety device should be incorporated to switch off the gauge filament and electrode supplies. Oxide-coated cathodes (used in the Edwards High Vacuum ionization gauge, IG2) which run at considerably lower temperature than tungsten, are preferred by some workers because they withstand better any in-rush of air; against this, such cathodes are more readily poisoned than tungsten, which, if it is contaminated, can be readily cleaned by 'flashing'. A filament of rhenium is recommended by Hall (H9).

3.10. The Cold-cathode Ionization Gauge; The Penning Gauge

The Penning gauge (P3) consists of two plate electrodes, P and P_1, set parallel to one another at a distance of about 1 in., joined electrically and used as a cathode with, between them, a ring-shaped anode, R (Fig. 3.24(*a*)).



(*a*)

(*b*)

FIG. 3.24 The Penning cold-cathode ionization gauge

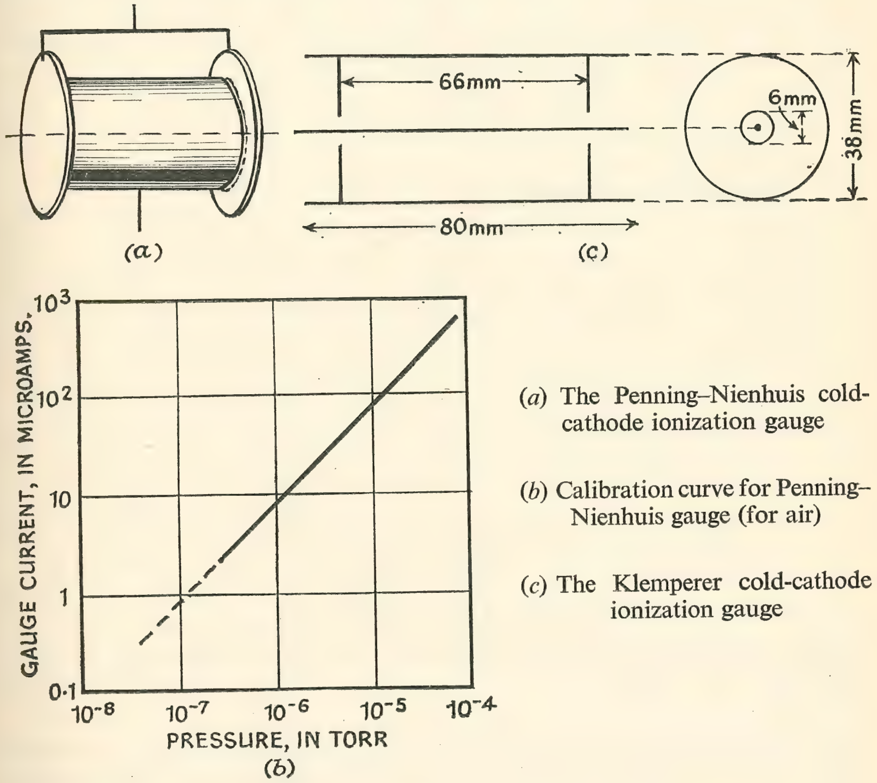
A steady p.d. of about 2 kV is maintained across the anode and cathode, supplied usually from a half-wave rectifier with a safety resistor of about 1MΩ in series (Fig. 3.24(*b*)). A permanent magnet (usually in the form of curved Alnico pole-pieces which fit over the tubular glass envelope in a clamp) is arranged to provide a magnetic flux density of about 400 gauss with the lines of force directed substantially perpendicular to the two cathodes. Electrons originating on positive ion collision at either of the cathodes are constrained by the magnetic field to pass through the open ring-anode rather than to move directly to it. The electron paths, not initially normal to the anode-ring plane, are helical owing to the action of the magnetic flux. Most of the electrons will consequently execute several paths to and fro about the anode ring before they are finally collected at the anode. In doing so, the trajectories through the gas in the gauge are much longer than if no magnetic field were present, and the probability that they will ionize gas molecules on collision is consequently much greater. Such ionization on collision is therefore possible down to pressures of 10^{-5} torr, which is 100 to 1000 times lower than with no magnetic field.

The calibration graph of the series ionization current recorded (using a microammeter with a full-scale deflection of 100 μA, provided with a shunt for 1 mA or 5 mA) is practically linear over the region from 10^{-5} to 10^{-3} torr, where this current is about 1 mA at the higher pressure. The maximum of the pressure range is usually at 5×10^{-3} torr.

Penning and Nienhuis (PN2) extended the lower pressure range to below 10^{-6} torr in a later design (Fig. 3.25(*a*)) which gave a current of about 1 mA at 10^{-4} torr (Fig. 3.25(*b*)) and was, furthermore, more free from the occasional current fluctuations which mar the working of the earlier instrument. This later design has the anode in the form of a cylinder extending almost to the cathodes so that the discharge is virtually enclosed within a box. A higher magnetic flux density of 1000 gauss was used, though Leck and Riddoch (LR1) report that a gauge of this type has a sensitivity practically independent of the flux density between 500 and 1000 gauss.

Klemperer (K5) introduced a cold-cathode gauge of a quite different electrode geometry in which a cylindrical cathode was used with an axial wire anode (Fig. 3.25(*c*)). This was operated in a magnetic field of flux density 250 gauss with the lines of force parallel to the anode wire (*i.e.* perpendicular to the electric field instead of substantially parallel, as in the Penning gauge) and provided by a solenoid (the authors have also used a cylindrical Alnico magnet). To eliminate disturbances due to electrostatic charges on the glass envelope walls, the cathode was enclosed at each end by diaphragms which had central apertures to permit entry of the anode wire. Klemperer found that for relatively high discharge currents the gauge absorbs appreciable amounts of gas in an uncontrollable manner. He therefore operated the gauge by varying the anode voltage (from 0·5 to 10 kV) to produce a constant small ionization current of 10 μA as the pressure was varied. A calibration curve obtained by Baker (B6) for this type of gauge is given in Fig. 3.26. The gauge works satisfactorily down to 10^{-6} torr and even to 10^{-7} torr. The central anode wire was of thoriated tungsten; this probably helped the initiation of the discharge at the lower pressures (a difficulty sometimes experienced with cold-cathode gauges) as a small number of α-particles are emitted from the thorium. Leck (L3) reports on the difficulty of initiating a discharge in cold-cathode gauges of the Penning type, and mentions that Evans and Burmaster (EB1) used a sharp-pointed electrode attached to the cathode to provide an initial supply of electrons by virtue of field-emission. Leck also states that in his own experiments with a Penning–Nienhuis gauge constructed with nickel electrodes (1 in. dia × 1 in. long) no initiation difficulties were experienced when using an h.t. supply of 3 kV.

Broad (B7) has described a gauge similar to that of Klemperer but where one end of the cylindrical cathode is left open (*i.e.* no enclosing diaphragm is used) and the anode wire at that end is pointed. The omission of one of the end diaphrams avoids a difficulty experienced with the Klemperer gauge: that gas flow from within the cylindrical cathode to the gauge tubulation is restricted by the low conductance of the diaphragm apertures, *i.e.* the Broad model can be a 'high-speed' gauge whereas the Klemperer pattern cannot.



(*a*) The Penning–Nienhuis cold-cathode ionization gauge

(*b*) Calibration curve for Penning–Nienhuis gauge (for air)

(*c*) The Klemperer cold-cathode ionization gauge

FIG. 3.25

Beck and Brisbane (BB2) have also designed a gauge on the Klemperer pattern but in which the use of baffle plates within the cylindrical cathode increases the gauge sensitivity.

The Broad and Klemperer type gauges operate very satisfactorily as alternatives to the Penning type.

Beer (B8) discusses the operation of a Penning gauge with an alternating voltage across the electrodes.

Conn and Daglish (CD1) have investigated the characteristics of cold cathode gauges of various electrode geometries.

The Penning gauge and developments therefrom form valuable instruments for the recording of pressures in the range from 5×10^{-3} down to 10^{-5} or 10^{-6} torr and are much used on vacuum plant where an accurate measurement of the pressure is not so important as information that the pressure is below a certain level, *e.g.* in vacuum coating apparatus.

Though incapable of recording pressures as low as is possible using modern forms of the hot-cathode ionization gauge, Penning gauges afford two important advantages in practice: (*a*) there is no thermionic filament to be poisoned or burnt out; (*b*) the associated electrical equipment is simpler.

The electrode structure of these cold-cathode gauges is usually fabricated from nickel. As sputtering (§ 10.10) will occur in the discharge, particularly at the higher pressures, appropriate glass shields should be included around lead-in wires to the electrodes to prevent deposited metal films from introducing electrical leakage. A gauge which has developed such a leak can be cleaned of deposited nickel by rinsing the interior with sodium hydroxide solution.

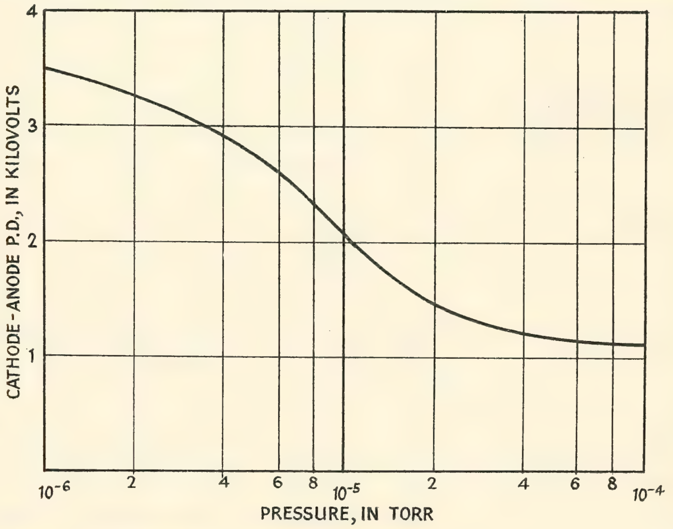


FIG. 3.26 Calibration curve for Klemperer gauge (for air)

Gauge current: 10 μA; magnetic flux density: 350 gauss; 1 MΩ resistor in series with gauge and h.t. supply

As the energy and density of the electrons in the cold-cathode ionization gauge are greater than in the hot-cathode counterpart, the rate of gas clean-up is considerably greater. Wide-bore tubulation is therefore important to avoid undue pressure differences between the gauge head and the vacuum tank. Leck (L3) reports on the clean-up action of the Penning gauge and gives values of the equivalent pumping speed for nitrogen and argon. All the common gases and water vapour are pumped.

These gauges cannot be degassed as readily as the hot-cathode types; indeed, rigorous degassing requires the use of an eddy-current heater. This is not, however, a serious disadvantage if the gauge is used as a pressure indicator down to 10^{-5} torr, but it adds considerably to the difficulty of making reliable pressure measurements at significantly lower values than this.

3.11. The Alphatron

This gauge is, in effect, an ionization chamber in which is registered the rate of formation of ions produced in the residual gas by a stream of alpha particles. Using a constant source of alpha particles (usually 0·2 mg of a gold–radium alloy in a sealed capsule) the ionization current is directly proportional to the gas pressure over a wide range. The original design is due to Downing and Mellen (DM1); the main features of their gauge are shown in Fig. 3.27(*a*). A p.d. of 30 to 40 V is maintained across the pair of grids shown and the ionization current produced is recorded. For air at 1 torr, the current is 2×10^{-10} amp. A d.c. amplifier is therefore necessary to enable a panel-mounted microammeter to be used and calibrated in pressure units. The first stage of this amplifier is usually built into the top of the gauge casing. The original alphatron had a linear response from 10^{-3} to 40 torr. Subsequently developed commercial models (National Research Corporation, in U.S.A. and Vacuum Industrial Applications Ltd., in Scotland) are of two types, one (Model 510; mains-operated) with a range from 10^{-3} to 10 torr (Fig. 3.27(*b*) shows the calibrations for a number of gases and vapours) and the other (Model 511; battery-operated) with the extraordinarily wide range from 10^{-4} to 1000 torr.

The long life, wide range and linearity of the alphatron make it a very valuable instrument for pressure recording. The chief objection to its wide-scale use is probably its price and it is not a type of instrument which can be readily constructed in the laboratory. Shielding (easily arranged) against the radioactive radiations is necessary.

The amplifier drift is reported by the manufacturers to be negligible after 10 min operation. The calibration for various gases is remarkably constant for a given gauge and can be reliably referred to if the nature of the residual gas in the vacuum system is known. The rate of gas clean-up by this gauge is negligible since the ionization currents obtained are small.

Beynon and Nicholson (BN1) give details of a design of radioactive ionization gauge which they used for measuring latent heats of vaporization. The pressure range of this gauge was from 10^{-5} to 10 torr.

The Analysis of Residual Gases

In addition to the measurement of the residual pressure in a vacuum system there is an increasing need to determine which gases and vapours are present. Apart from the value of such information in research, it is invaluable in several cases of industrial practice, *e.g.* in the manufacture of electron tubes, in vacuum metallurgy, in studies of the outgassing of materials and in leak detection (§ 9.9). The mass spectrometer is an important instrument for this type of analysis, the purpose of which is to separate the ionized molecules of the gas according to their various mass/charge ratios. There are several kinds of mass spectrometer which are applied to a wide variety of analytical problems in chemistry, physics and metallurgy as well as to those of vacuum technology (Barnard, B9) but they all have certain features in common.

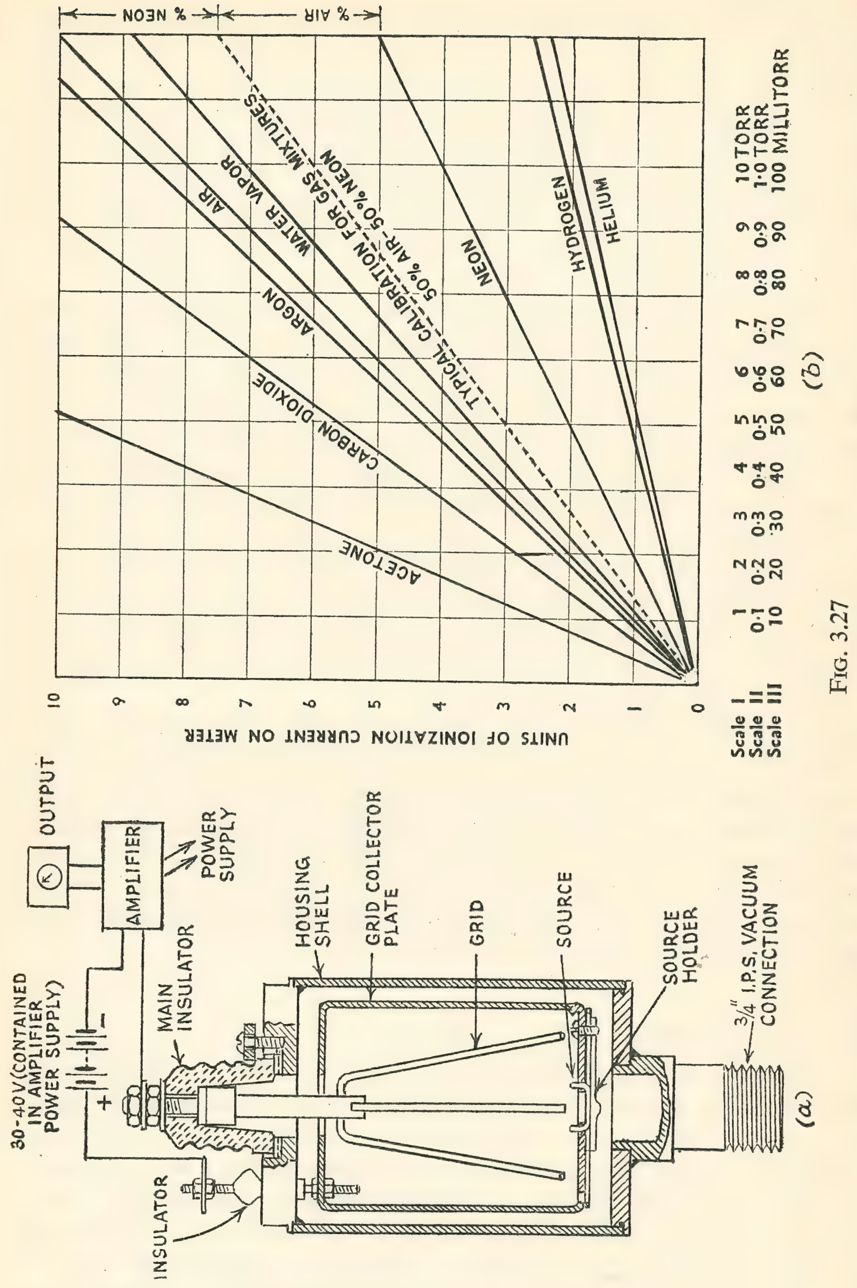

30-40V (CONTAINED IN AMPLIFIER POWER SUPPLY)
+
−
OUTPUT
AMPLIFIER
POWER SUPPLY
MAIN INSULATOR
INSULATOR
HOUSING SHELL
GRID COLLECTOR PLATE
GRID
SOURCE
SOURCE HOLDER
3/4" I.P.S. VACUUM CONNECTION
(a)
% NEON
% AIR
UNITS OF IONIZATION CURRENT ON METER
0
1
2
3
4
5
6
7
8
9
10
ACETONE
CARBON DIOXIDE
ARGON
AIR
WATER VAPOR
TYPICAL CALIBRATION FOR GAS MIXTURES
50% AIR - 50% NEON
NEON
HYDROGEN
HELIUM
Scale I 1 2 3 4 5 6 7 8 9 10 TORR
Scale II 0·1 0·2 0·3 0·4 0·5 0·6 0·7 0·8 0·9 1·0 TORR
Scale III 10 20 30 40 50 60 70 80 90 100 MILLITORR
(b)

FIG. 3.27

(*a*) The alphatron gauge (*Downing and Mellen*)
(*b*) Calibration curves for alphatron gauge (*Vacuum Industrial Applications Ltd.*)

These are (*a*) an ion source; (*b*) a mechanism for sorting out ions according to their mass/charge ratio; (*c*) a means of detecting the ions. The chief difference between the various types is with regard to (*b*); two main principles are used: either the ions are accelerated and then passed through a magnetic and/or electrostatic field, in which their trajectories depend upon their mass/charge ratio, or the ions are accelerated and, in effect, the time they take to traverse the distance between two specific locations is determined, which time is also dependent on the mass/charge ratio for the ion concerned. The first class of instrument is a deflection mass spectrometer; the second class, a time-of-flight mass spectrometer.

3.12. Magnetic Deflection Mass Spectrometers

Of the various kinds, that which has been most frequently used in vacuum technology is the **Nier mass spectrometer** (N3). In this instrument, the gas is ionized, the ions are accelerated by an electrostatic field, and are then deflected by a magnetic field through an angle of 60°, 90° or 120°. Previous to Nier, the pioneer work of Dempster (D4) is important; the **Dempster mass spectrometer** may be classed as one in which the angle of deflection in the magnetic field is 180°. Developments from this early work of Dempster have been much used in recent 180° instruments, especially in leak detection practice (§ 9.9).

The essential features of the Nier mass spectrometer are shown in Fig. 3.28(*a*) where the angle of deflection is 60°; Fig. 3.28(*b*) is shown for comparison where the angle is 180°.

The ion source used is either a hot-cathode or cold-cathode device. The Nier ion source is of the former type. The positive ions produced are accelerated by the p.d. V between the slits S_1 and S_2 to enter the analysing magnetic field of strength H. Within this field, the radius of curvature ρ of an ion of mass m and charge e is given by:

$$\frac{mv^2}{\rho} = Hev \tag{3.15}$$

where v, the velocity of the ion, is decided by the potential difference V in accordance with the equation:

$$\tfrac{1}{2}mv^2 = Ve \tag{3.16}$$

Substitution for v in equation (3.15) from equation (3.16) gives

$$\rho = \frac{\sqrt{2Vm/e}}{H}$$

If it is assumed that the ion is singly charged, *i.e.* e is the electronic charge ($1{\cdot}6 \times 10^{-20}$ e.m.u.) then

$$\rho = \frac{\sqrt{2V \times 10^8 m/1{\cdot}6 \times 10^{-20}}}{H} = \frac{1{\cdot}118 \times 10^{14}\sqrt{Vm}}{H}$$

where V is in volts, H is in gauss and m is in grams. It is more convenient to express the mass of the ion in terms of its molecular weight, M, referred to the atomic weight of oxygen as 16. As the mass of the oxygen atom is $2{\cdot}656 \times 10^{-23}$ gram, the equation for ρ becomes:

$$\rho = \frac{144}{H}\sqrt{VM} \tag{3.17}$$

If H is kept constant, ρ can be made a specific value for an ion of mass M by varying V the accelerating p.d.; ρ is decided by the entrance slit S_2 to the magnetic field, the slit S_3 within this field (which decides the ion beam width) and the outlet slit S_4 to the ion detector.

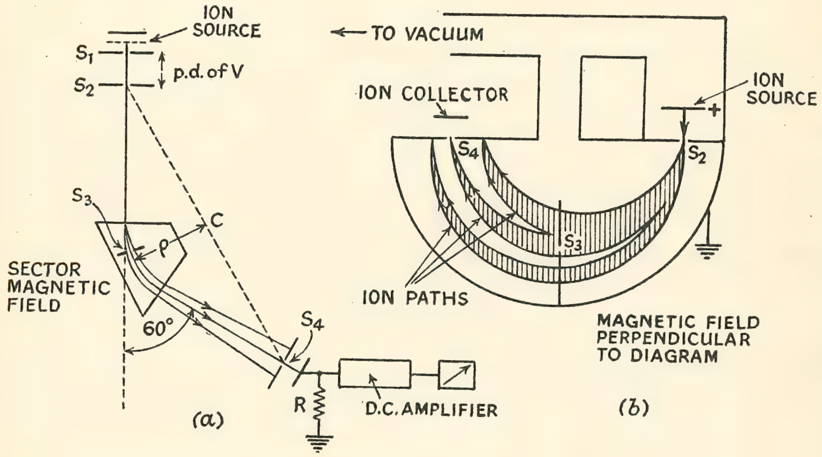


FIG. 3.28 Principles of (*a*) the Nier and (*b*) the Dempster mass spectrometers

It can be shown (Herzog, H10; Barber, B10; Stephens, S7) that a mono-energetic ion beam will be focused at a point (or short line) at the slit S_4 by the action of the magnetic field provided that the central ray of the ion beam is normal to the boundary where it enters the field and where it leaves it and provided also that the slit S_2, the centre of curvature C of the trajectory of the ion in the magnetic field, and the outlet slit S_4, lie on the same straight line. This condition is satisfied by the 60° sector magnetic field in the Nier instrument if the source produces monoenergetic ions which traverse field-free space before entering and after leaving the magnetic field. It can be seen to apply also in the 180° deflection case.

The ions with a specific radius of curvature ρ arrived at by altering the p.d. V for a given value of H will traverse the outlet slit S_4. To measure the ion current, the ion collector electrode is connected to earth via a high value resistor R. The p.d. produced across R is then made the input to either an electrometer valve in a stabilized circuit followed by a d.c. amplifier and output meter or a vibrating reed electrometer.

A plot of ion current against the p.d. V can therefore be obtained. The instrument can be calibrated by introducing gases to the ion source of known atomic weight, *e.g.* oxygen, argon and helium, and hence the graph can be converted to one of positive ion current against ion mass *i.e.* a mass spectrum is obtained. The resolving power of the instrument is defined as m/dm, where dm is the mass separation distinguishable at a mean mass m. To define what is meant by 'distinguishable', the convention is to regard dm as the width of the trace obtained for a particular mass at half the peak height. The relative abundance of the ions of various masses present in the ion source can also be deduced as it is given by the corresponding relative peak ion currents.

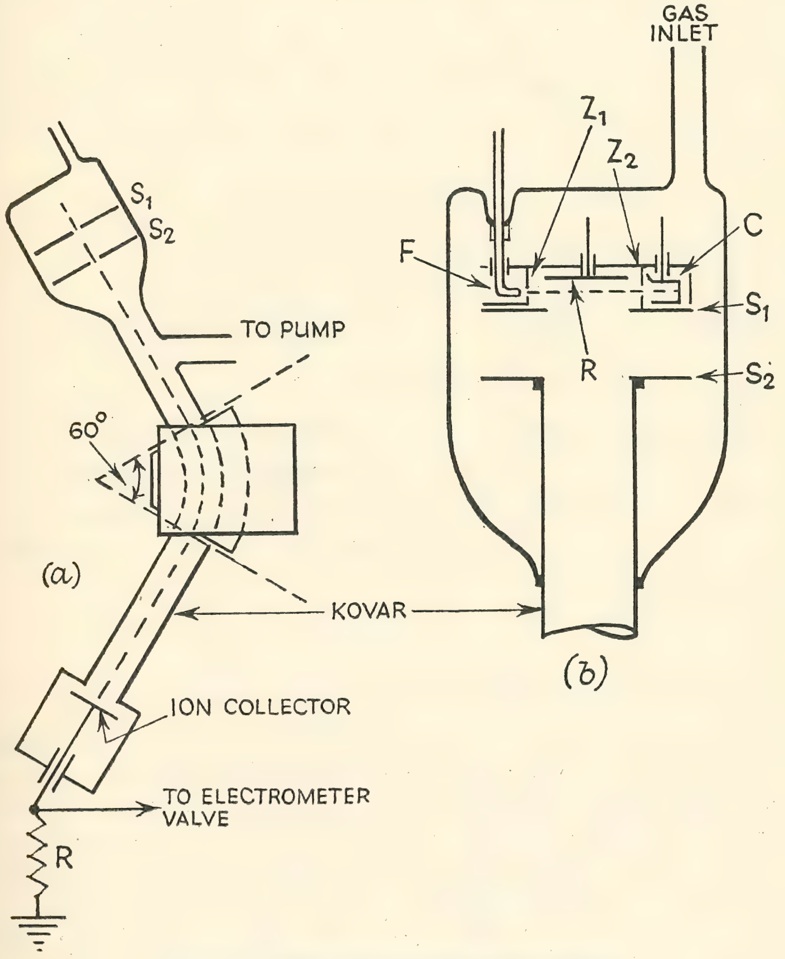


FIG. 3.29 The Nier 60° mass spectrometer

A more detailed diagram of the Nier 60° mass spectrometer (Fig. 3.29(*a*)) shows the type of hot-cathode ion source used (Fig. 3.29(*b*)). The object of this design of ion source, which has been widely used, is to produce all ions under similar energy conditions in the same plane in the gas. To achieve this, electrons emitted from the heated ribbon filament F are accelerated to a defining slit Z_1 (about $2{\cdot}5 \times 0{\cdot}2$ mm) at about 100 V positive with respect to the filament, and then travel with constant energy to a second slit Z_2 (about

5 × 1 mm) at the same potential. To increase the electron paths and so the ionizing efficiency and also to confine the electrons to the region between the slits, an auxiliary magnetic field provided by a pair of Alnico pole-pieces is directed along the electron beam. Those electrons which tend to leave the beam are then made to execute tight helical paths across the gas between the slits Z_1 and Z_2. On emerging from Z_2, the electrons enter the trap C which is at a slightly more positive potential than Z_1 and Z_2 and where the electron current is monitored. Below the strip of ions produced in the wake of the electron beam is the pair of parallel aligned slits S_1 and S_2. Across S_1 and S_2 is maintained the p.d. V (variable from about 500 to 1200 V) with S_2 negative with respect to S_1 (in practice, S_2 is earthed). This p.d. V is supplied by a power pack stabilised to have a voltage variation at any particular setting of not more than about 1 part in 50,000.

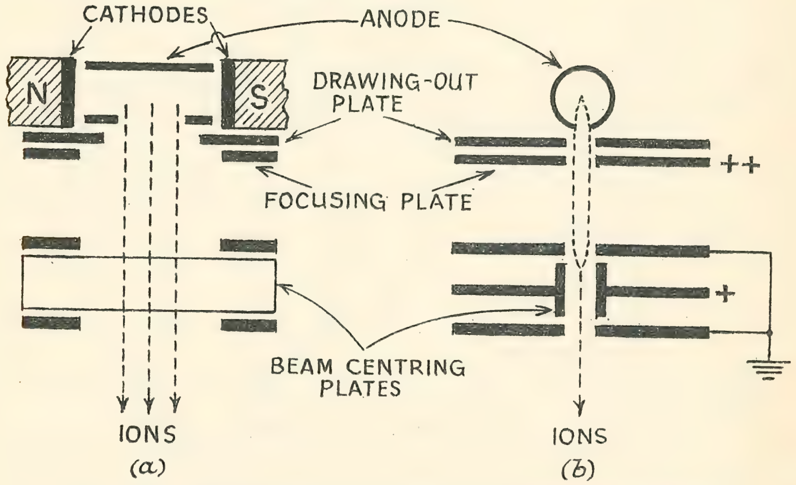


FIG. 3.30 A cold-cathode ion source for a mass spectrometer

The positive ions created in the region of the electron beam are repelled towards the slit S_1 by the action of a small positive potential (so-called 'walking potential') on the repeller plate R. The ions are then accelerated by the electric field between the slits S_1 and S_2 to leave S_2 as a monoenergetic beam. They travel in straight lines in field-free space until they enter the main analytical field in which the trajectories have radii of curvature decided by equation (3.17). As ρ is fixed by the location of the slits S_3 and S_4 (Fig. 3.28(*a*)) only those ions of a specific molecular weight M will reach the final ion collector for a given value of the p.d. V.

A variety of hot-cathode ion sources designed for mass spectrometers has been described in the literature (e.g. Barnard, B9; Nier, N3; Plumlee, P4; Inghram and Hayden, IH1).

Cold-cathode ion sources have also been employed with the advantage that burn-out of a thermionic filament is not troublesome, but with the considerable disadvantage that the energy spread of the ions is about 20 eV (Backus, B11) so that the resolving power provided by the mass spectrometer is small.

These sources are similar to a Penning gauge (§ 3.10) in that the gaseous discharge is operated in a magnetic field. Simple designs are given by Guthrie and Wakerling (GW1) and by Milner (M4). Fig. 3.30 illustrates schematically a cold-cathode ion source described by Inghram and Hayden (IH1). In general, such ion sources are used for mass spectrometers intended for leak-detection, where limited resolving power is adequate (§ 9.9), rather than for general analytical work.

The ion collector may be of the simple type (Fig. 3.31(*a*)) or the suppressive type (Fig. 3.31(*b*)) (Berry, B12; Barnard, B9; details are also given by Giorgi, G5). In the simple type, the form of the collector cup is such as to reduce reflection of the ions. An electrode containing a slit is inserted between the defining entry slit and the collector and maintained negative with respect to the entry slit to suppress secondary electrons. In the suppressive type of ion collector, an ion suppressor slit provides a potential barrier so that low energy ions are not collected. This prevents the collection of low energy ions which may be produced in the region beyond the analysing field by collision of ions in the focused beam with residual atoms and molecules in the residual gas. This is particularly necessary if the gas pressure in the mass spectrometer is high, *e.g.* in leak detection practice (§ 9.9).

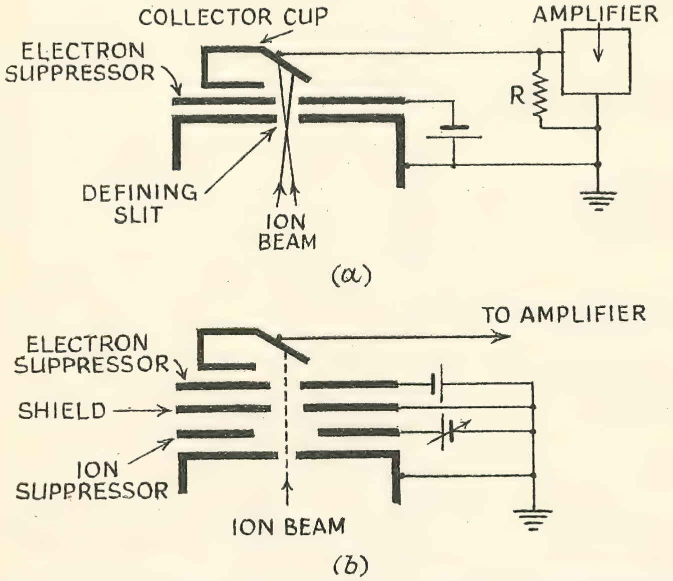


FIG. 3.31 Ion collectors for mass spectrometers: (*a*) simple type; (*b*) suppressive type

The ion collector currents encountered are, in general, in the range from 10^{-18} to 10^{-8} amp.

The A.E.I., mass spectrometer, type MS3, is designed for the analysis of mixtures of gases or volatile liquids and isotope abundance ratio determinations in the low mass range. It is a 90° sector type instrument. Electromagnetic scanning by variation of the magnetic field produced by the electromagnet or electrostatic scanning by variation of the ion-accelerating voltage over the range from 500 to 200 V may be used. A mass range from 2 to 130 may be covered with a mass resolution of from 40 to 150 depending on the adjustment of the collector slit width. For normal operation this slit is adjusted to give a resolution of about 100. The standard gas sample is about 1 cu cm at S.T.P. which is expanded into a reservoir vessel of 2 litre volume; gas concentrations as small as 0·01% can then be observed. Smaller samples with volumes down to 0·01 cu cm can be analysed if a reservoir of smaller volume is used. The use of an automatic recorder of the amplified ion current enables continuous monitoring of gas samples to be undertaken. This firm also markets a double focusing mass spectrometer (Type MS7) of the Mattauch type (M5) for the analysis of solids. To produce the necessary positive ions characteristic of the solid, a spark is set up between two electrodes of the sample material placed close together in vacuum. Photographic recording is usually employed but the collected ion currents can also be monitored. The complete mass spectrum from lithium (mass numbers 6 and 7) to uranium (mass numbers 234 to 238) can be obtained in a single exposure on a 10 in. photographic plate, the sensitivity being down to 1 part in 10^8 atoms. Mass 238 is recorded at the maximum ion accelerating potential of 20 kV with a magnetic field strength of 15,400 gauss whereas to record mass 5 the field strength is reduced to the minimum value of 2200 gauss.

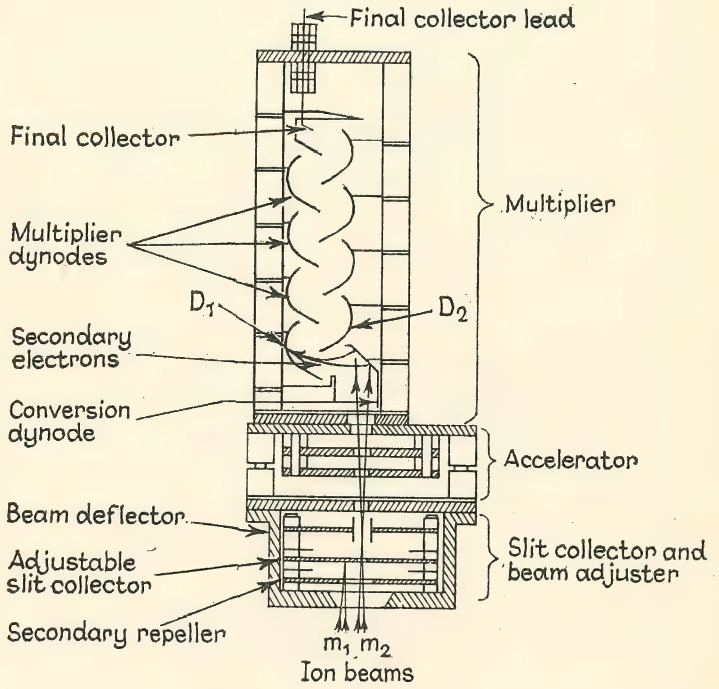


FIG. 3.32 Use of an electron multiplier to record the positive ion currents in a mass spectrometer

A method of recording the positive ion current which has been developed more recently is to use an electron multiplier. Reynolds (R7) has employed this type of detector to record the partial pressures in an ultra-high vacuum system at a total pressure of 10^{-10} torr and states that he was able to record the presence of only 5×10^5 atoms of xenon. The principle concerned is illustrated by Fig. 3.32. The target or conversion dynode on which the positive ions impinge is usually made of manganese silver; the electrons released from this target are accelerated and guided towards the first dynode D_1 by the electrostatic field between D_1 and the conversion dynode; the secondary electrons released from D_1 are then accelerated and directed towards the succeeding dynodes D_2 and so on via D_3 to D_9 (or even to D_{14}) to give eventually an output current at the final collector. As the ratio m of the number of secondary electrons to the number of primary electrons is greater than unity (about 2·5) at each dynode, the overall gain possible is several thousand.

The electron multiplier detector has remarkable sensitivity and is valuable when rapid recording of small currents is required, but its response is non-linear. However, the sensitivity is too high for convenient working with the larger incident positive ion currents, so this method is used when the total residual pressure in the mass spectrometer is about 10^{-8} torr or less. This demands, of course, a system which can be thoroughly degassed by baking. At present, a number of laboratories have set up such mass spectrometers for studies of gas constituents in the ultra-high vacuum range (*i.e.* pressures $< 10^{-7}$ torr, *see* Chapter 8). Warmoltz and Greft (WG1) have used an instrument of this type in leak detection (§ 9.10).

Space does not permit a survey of the many recent reports on the use of deflection type mass spectrometers in analysing the residual gases in vacuum systems (*see* Edwards, E1; Hintenberger and Dörnenburg, HD1; Giorgi, G5). In general, an instrument with a resolving power of 100 is adequate for most investigations, as the gases and vapours concerned do not usually have mass numbers exceeding 60. The first important work in this field was undertaken by Blears (B13). He used three mass spectrometers each basically similar to the Nier 60° instrument: (*a*) with an envelope of borosilicate glass and copper and entirely free from demountable joints and evacuated by a mercury diffusion pump system; (*b*) constructed chiefly of brass; (*c*) made principally of steel. In cases (*b*) and (*c*), several rubber gasket joints were used and the main vacuum system utilized an oil diffusion pump. Fig. 3.33 shows part of the mass spectrum obtained with the brass mass spectrometer where the diffusion pump was filled with Apiezon C oil. The high percentages of hydrogen and water vapour are significant as also are the hydrocarbons which, without a cold trap, were recorded up to mass numbers of several hundred. In this spectrum, the black parts of the trace were obtained when a cold trap at $-78°$ C (solid carbon dioxide) was used, whereas the white parts show the increases on raising the trap temperature to 20° C. In experiments with the stainless steel mass spectrometer, it was opened to the atmosphere for about 3 hours and then evacuated, but without baking or using cold traps. After pumping for about 60 min, only 0·5 of the gas phase was air, some 70% of the ions present were formed from water, and most of the remainder were hydrocarbon vapours. Blears further states that 'the time constant for removal of residual molecules, deduced from the observed rate of fall of pressures, was only 1/4000 of that calculated from the volume of the system and the speed of the diffusion pump'. This is because the rate of removal of vapour and gases from the vacuum system, after the initial pump down, is decided by the forces which bind the molecules (chiefly water vapour) to the surfaces within the vacuum vessel. Further prolonged pumping gradually reduces the water vapour content, but the amount of hydrocarbon—from the pump fluid—does not fall below a certain limit.

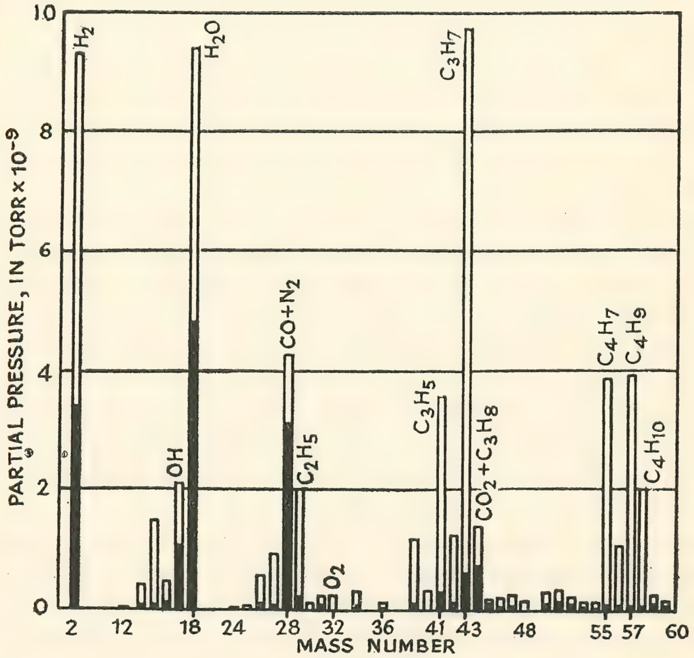


FIG. 3.33 Mass spectrum of the residual gases in a mass spectrometer constructed chiefly of brass and exhausted by an oil diffusion pump (*after Blears*)

Table 3.4 gives the partial pressures recorded by Blears at the ultimate pressure after several weeks operation with bakings for at least 48 hours using three different pumping fluids: mercury, Apiezon BW and Apiezon C. The value of baking at the highest possible temperature is amply demonstrated. The most abundant residual is water, even in trapped systems, except for mercury when a mercury diffusion pump is used (the high mercury vapour pressure would seem to indicate that Blears' cold trap was not very efficient even when filled with liquid air, *see* § 8.1). Residual hydrocarbons are generally more prevalent in oil pumped systems. The presence of these hydrocarbons when using a mercury diffusion pump is explained on the basis that oil molecules from the rotary pump diffuse through the system in the initial stages of evacuation before the diffusion pump is switched on, demonstrating the desirability of including a trap between the rotary pump and the diffusion pump. The presence of carbon monoxide is due to the formation of tungsten carbide on the hot tungsten filament (of the ion source or attached ionization gauge) when operated in hydrocarbon vapour. The carbide in the presence of water vapour in the system produces carbon monoxide. If water vapour or hot filaments are eliminated from pumped systems, very little monoxide is detected.

TABLE 3.4
Partial pressures (in units of 10^{-9} torr) of the constituents of the residual gas at the ultimate pressure

Pump fluid	Mercury			Apiezon BW		Apiezon C	
Bake-out temp. in °C	100	250	100	100	100	100	100
Trap temp. in °C	−78	−78	−170	−78	20	−78	20
Hydrogen	—	—	—	3	22	4	9
Water	19	2·2	6·0	7	25	4	9
Carbon monoxide	9	0·1	1·0	1·1	—	3·1	2·5
Air	1·0	0·5	1·8	1·6	—	0·5	1·5
Carbon dioxide	1·3	0·1	1·7	0·5	12	0·9	1·8
Σ CH	4	1·2	1·3	5	1250	10	60
Mercury	205	224	15				

Further important studies using a mass spectrometer have been made by Hannay (H11) and by Morrison (M6) of the residual gases present in electron tubes.

The perfect focusing properties of crossed magnetic and electric fields have been employed in the **trochotron** type of mass spectrometer (Robinson and Hall, RH1; Perkins and Charpentier, PC2). This type of instrument has not yet reached full development and has not yet been made commercially available, but it shows considerable promise as an analytical tool because large ion beam currents may be employed with high resolving power.

3.13. Time-of-flight Mass Spectrometers

There are three main types of instrument in which ions of different mass/charge ratios are separated by virtue of the different velocities imparted to them and where the ions consequently take different times to travel over a given path. These types are: (*a*) pulsed beam analysers; (*b*) radio frequency mass spectrometers and (*c*) the omegatron.

In **pulsed beam analysers**, a short pulse of monoenergetic ions (containing ions of various mass/charge ratios) traverses a tube of length L; the transit time t of ions of a particular mass/charge, m/e, with velocity v is decided by:

$$t = L/v$$

If the p.d. through which the ions are accelerated initially is V, then:

$$v = \sqrt{\frac{2Ve}{m}}$$

$$\therefore \quad t = L/\sqrt{\frac{2Ve}{m}}$$

At the ion collector at the far end of the tube, ions will therefore arrive at times decided by m/e, the heavier ions requiring the longer times of travel. This principle has been applied to a number of designs of mass spectrometer, but the demand for pulses of ions of very short duration to give adequate resolving power has limited their application so far.

Radio frequency mass spectrometers have been designed by Bennett (B14) and Redhead (R8). The general principle is illustrated by Fig. 3.34. Electrons from the thermionic filament F are accelerated to the grid G_1 which is at a positive potential V (about 150 V). The positive ions resulting from electron impact with the residual gas molecules are then accelerated between the grids G_1 and G_2 as the potential of G_2 is maintained negative (it is earthed) with respect to G_1. These ions enter continuously the analyser A consisting of three equally spaced grids G_3, G_4 and G_5. The outer grids G_3 and G_5 are earthed whereas the central grid G_4 has an r.f. alternating potential applied to it with respect to earth. Beyond this analyser is the ion collector electrode C which is earthed via the high value resistor R. In front of this collector is a grid G_6 at a positive potential V_R, $(=V)$ with respect to earth. For ions to reach C they must surmount this retarding potential V_R. Whether or not they are able to do so depends on whether they gain or lose energy as they traverse the alternating field between the analyser grids G_3, G_4 and G_5, which will be decided by their time of arrival (*i.e.* phase) at the grid G_3 in relation to the instantaneous potential at that time on G_4. Those ions which do gain energy can be shown to do so to the maximum extent when

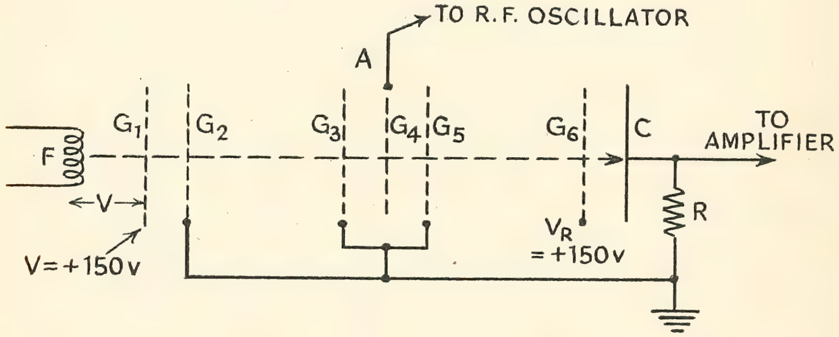


FIG. 3.34 Principle of the Bennett type of radio frequency mass spectrometer

$$\left(\frac{2\pi fs}{v} + \theta\right) = n\pi$$

where s is the separation between G_3 and G_4, equal to that between G_4 and G_5, f is the frequency of the r.f. supply to grid G_4, v is the velocity of the ions (decided by V in relation to e/m for the ion), θ is the phase angle of the alternating p.d. on G_4 at the instant the ions pass G_3, and n is an integer.

The mass/charge ratio of the ions which acquire this maximum energy is given by:

$$\frac{m}{e} = \frac{0{\cdot}266V}{s^2f^2}$$

The chief application in vacuum technology of this type of tube has been in the development of a leak detector of remarkable sensitivity by Varadi and Sebestyén (VS1), *see* § 9.10.

Of considerable current interest as a gas analyser in vacuum practice is the **omegatron,** particularly as it is small, comparatively inexpensive, and can be thoroughly degassed on the vacuum system. This interesting device is based on the principle of the cyclotron. As is well known, the time T taken by an ion of mass/charge ratio, m/e, to execute a single revolution within the dees of a cyclotron is given by:

$$T = \frac{2\pi m}{He}$$

where H is the uniform magnetic field perpendicular to the plane of the ion orbit. To ensure continuous acceleration of these ions over their whole path from the centre to the edge of the dees, T must also be the period of the alternating p.d. applied across the dees. Hence ω, equal to $\frac{2\pi}{T}$, the pulsatance of this supply, is decided by:

$$\omega = \frac{He}{m} \tag{3.18}$$

For a given value of H, the pulsatance of the a.c. supply is directly proportional to m/e.

The omegatron was first described by Sommer, Thomas and Hipple (STH1) though most of the instruments which have been designed specifically for the analysis of the residual gases in vacuum systems are based on the simplified version due to Alpert and Buritz (AB1). This consists basically (Fig. 3.35) of a pair of parallel flat plates PP_1 (corresponding to the dees of a cyclotron) with a surrounding shield box B. Electrons from the thermionic filament F are accelerated through an aperture A_1 in the box wall to produce a beam A_1A_2 along the axis symmetrically between the plates PP_1. This electrode construction, forming a 1 cm or 2 cm cube, is within a glass envelope (connected to the vacuum system) which is mounted between the poles of a magnet so that a uniform field H of about 2000 gauss, and with a cross-section at least equal to that of the box, is directed along the electron beam. With an r.f. potential across the plates PP_1, the alternating electric field E is then perpendicular to the constant magnetic field. With a positive potential on the box of about 100 V with respect to the filament, the residual gas within the box is ionized by electron impact. The positive ions created will (as in a cyclotron) describe orbits in a plane perpendicular to the magnetic field lines. If the pulsatance ω of the alternating field between plates PP_1 is such that equation (3.18) is satisfied for ions of a particular value of m/e, these ions will describe a spiral path like that shown in Fig. 3.35 and eventually impinge upon the ion collector electrode C. The ionization current recorded at C will be a measure of the abundance of ions having this value of m/e in the ionization region. By varying the frequency of the alternating supply, ions of various values of m/e can be brought to the collector C and a mass spectrum obtained.

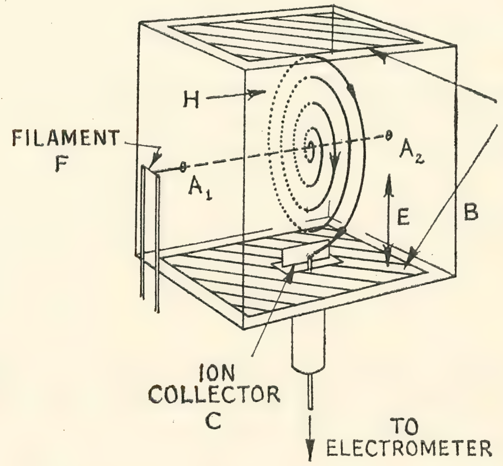


FIG. 3.35 Principle of the omegatron

The resolving power of the instrument can be shown to be given by (Berry, B15; Warnecke, W2; Amoignon and Rommel, AR1):

$$\frac{m}{dm} = \frac{RH^2}{2E_0}\frac{e}{m} \qquad (3.19)$$

where R is the maximum radius of the spiral, *i.e.* the distance of the ion collector from the electron beam axis, E_0 is the peak alternating p.d. across the plates, PP_1, and e is the ionic charge.

Fig. 3.36(*a*) shows the Alpert–Buritz design in detail. The r.f. plates (*i.e.* corresponding to PP_1 of Fig. 3.35) and the shield box (2 cm cube) are constructed from non-magnetic copper–nickel alloy (Advance) sheet. The ion collector electrode projects into the box through the lower r.f. plate. The lead from this collector is shielded by a cylinder anchored to the glass pinch and is brought out through the pinch via a highly insulated pin. The assembly is mounted within a glass envelope attached via tubulation to the vacuum system and the magnetic field is provided by a large permanent magnet with flat pole faces.

It is essential to degas the omegatron by bakeout at 450° C and the electrodes must be induction-heated to 900° C before using it at low pressures ($< 10^{-5}$ torr) for gas analysis, otherwise unstable operation will be experienced, in particular the resonant ion current will decrease with time. To ensure freedom from subsequent outgassing and the accumulation of electrically polarized gas films and surface films on the electrodes, the Leybold omegatron has electrodes (other than the filament) constructed from platinum–iridium alloy (E. Leybold's Nachfolger). Tantalum has also been used, but less successfully. The model due to Klopfer (K6) (Fig. 3.36(*b*)) has electrodes of platinum sheet and between the r.f. plates are arranged four guard rings to ensure a uniform electric field.

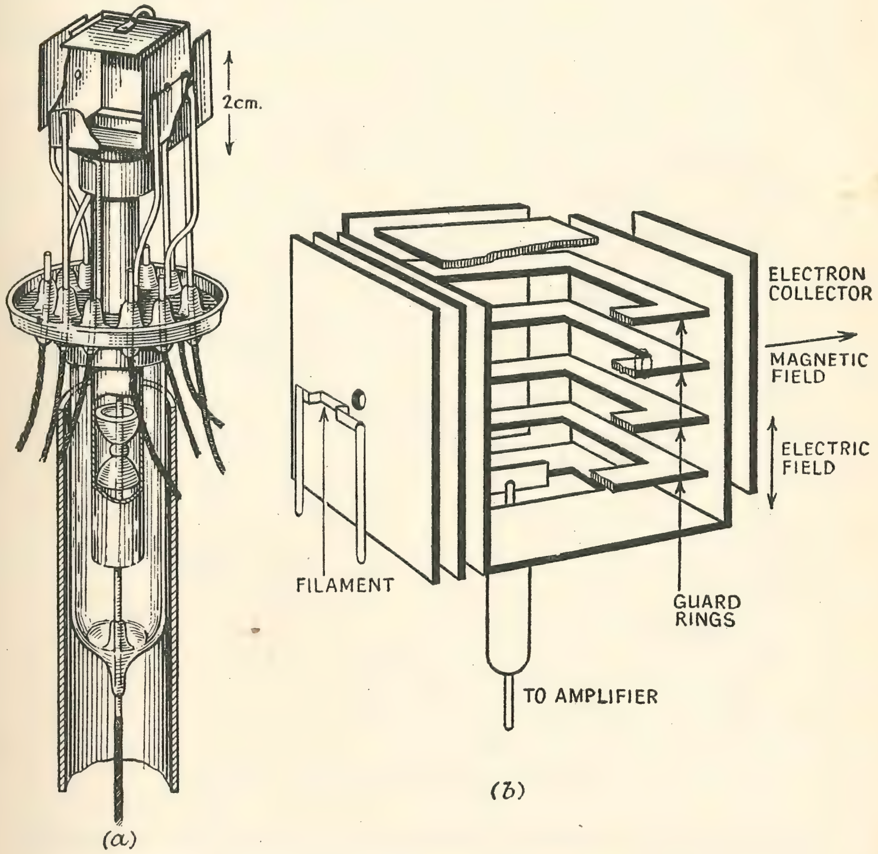


FIG. 3.36 Two designs of omegatron

(*a*) The Alpert–Buritz type

(*b*) The Klopfer type

Due to the components of the initial velocities of the positive ions in the direction of the electron beam, drift of these ions away from the interaction area tends to occur. As this results in a decrease of ion collector current at resonance, it is counteracted by a 'trapping field', the purpose of which is to minimize the effect of initial velocity components. This field is usually arranged by the application of a trapping potential on the box.

Warnecke (W2) gives a circuit for operating an omegatron of the Alpert–Buritz type. The r.f. generator must provide a stable e.m.f. variable from 0 to

2 V r.m.s. at a stable frequency over the range from 50 kc/s to 3 Mc/s. A small steady potential, known as the 'walking potential' is superimposed on the r.f. signal, the function of which is to remove non-resonant ions from the interaction region and so prevent undue build-up of positive space charge due to these ions. The trapping potential is applied to the box and is positive with respect to the r.f. plate which is at the minimum positive potential with respect to earth. The ion collector plate is earthed and the mean potential of the rest of the electrode assembly is slightly negative with respect to earth, the thermionic filament being at about —90 V. The ion collector currents are measured by a vibrating reed electrometer.

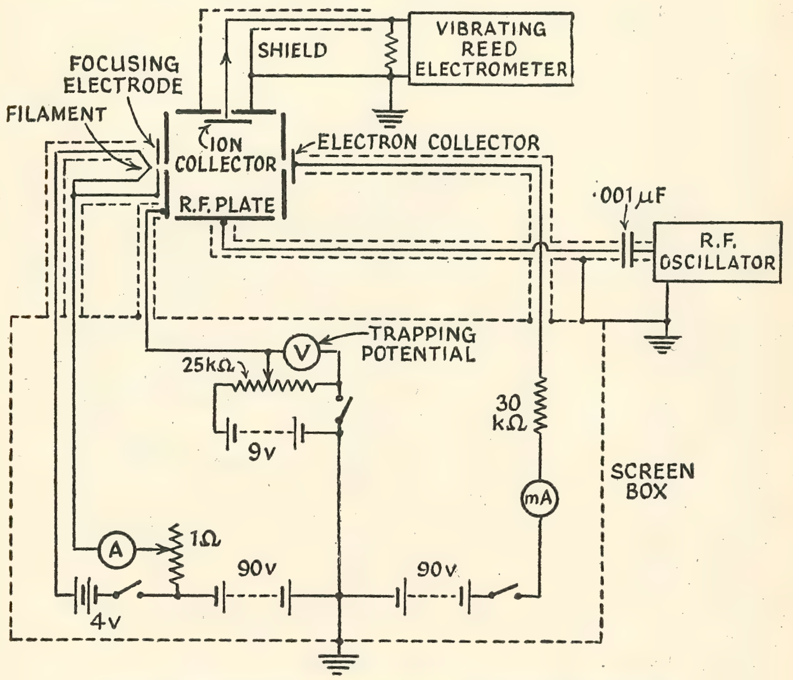


FIG. 3.37 Operating circuit for the Leybold omegatron

The circuit for the Leybold omegatron (Fig. 3.37) is simpler as one of the r.f. plates is earthed and, usually, no r.f. bias or ion collector bias is used.

Data supplied by the manufacturer states that the Leybold omegatron is operated within a magnetic field of strength 2100 gauss (careful line-up of this field relative to the electron beam direction is essential on setting up the instrument) and that, with the optimum trapping potential to obtain maximum ion current, the relative sensitivities for various gases compared with nitrogen as unity are as recorded in Table 3.5.

Giorgi (*private communication, see also* G5) has made an extensive study of the characteristics of the Leybold omegatron. His results (Table 3.6) were obtained with a magnetic field strength of 2600 gauss for helium, neon and argon; the figures for nitrogen are given by Leybold and apply to the conditions where the field strength was 2100 gauss.

TABLE 3.5

Characteristics of the Leybold omegatron: 1

Gas	Mass number	R.F. potential volt (r.m.s.)	Relative sensitivity
H_2	2	1·5	1·1
He	4	1·5	0·8
Ne	20	0·6	0·67
N_2	28	0·6	1·00
O_2	32	0·6	1·15
A	40	0·4	1·00
CO_2	44	0·4	0·74
Kr	84	0·4	0·52
Xe	132	0·4	0·26

TABLE 3.6

Characteristics of the Leybold omegatron: 2

Gas	Resonant frequency in kc/s		Energy of collected ions, eV	Resolving power	R.F. field volt/cm
	Calculated[1]	Measured			
He	990	965	65·7	36·5	1·0
Ne	197	195	13·1	9·7	0·75
N_2	114·2		6·4	8·9	0·4
A	99	95	6·5	7·3	0·5

[1] Using equation (3.18).

TABLE 3.7

Analysis of gases in kinetic all-glass system with mercury diffusion pump and liquid air trap (after Giorgi)

Mass number	Probable gas or vapour	Peak ion current normalized for an electron beam current of 1 μA
2	hydrogen	3×10^{-14}
14	nitrogen	4×10^{-13}
16	oxygen	1×10^{-13}
18	water vapour	1×10^{-13}
28	nitrogen and/or carbon monoxide	$1{\cdot}5 \times 10^{-12}$
32	oxygen	4×10^{-13}
40	argon	2×10^{-14}
44	carbon dioxide	3×10^{-14}

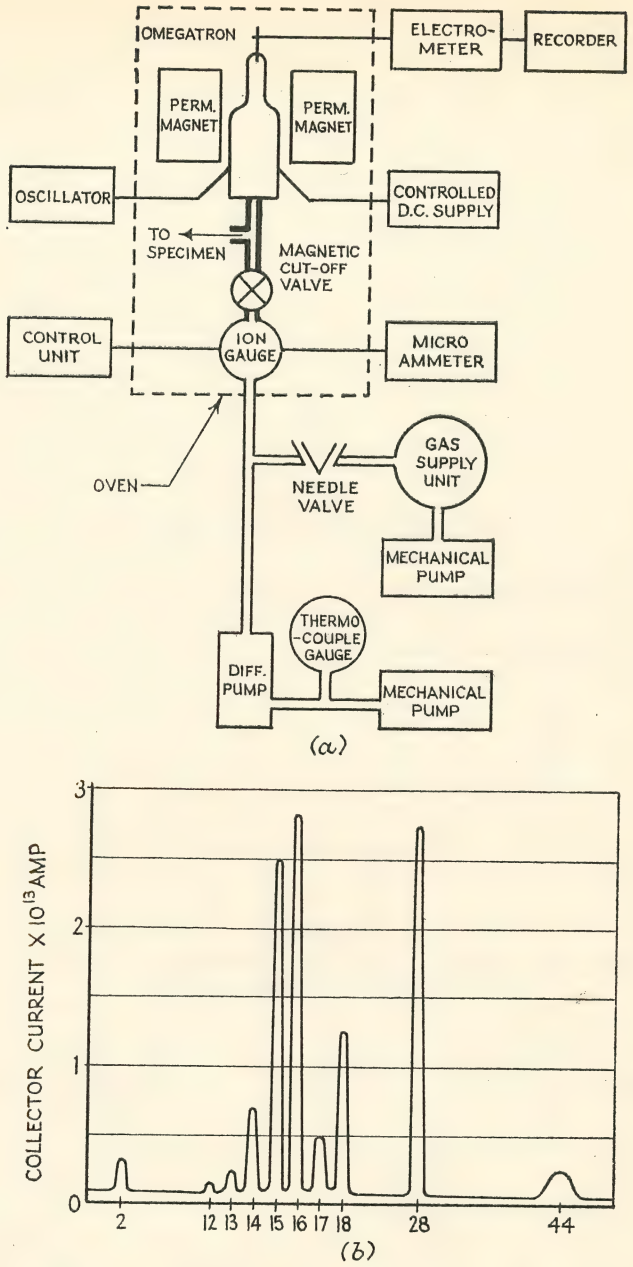

OMEGATRON
ELECTRO-METER
RECORDER
PERM. MAGNET
PERM. MAGNET
OSCILLATOR
CONTROLLED D.C. SUPPLY
TO SPECIMEN
MAGNETIC CUT-OFF VALVE
CONTROL UNIT
ION GAUGE
MICRO AMMETER
OVEN
GAS SUPPLY UNIT
NEEDLE VALVE
MECHANICAL PUMP
THERMO-COUPLE GAUGE
DIFF. PUMP
MECHANICAL PUMP
(a)
COLLECTOR CURRENT X 10^13 AMP
0
1
2
3
2
12
13
14
15
16
17
18
28
44
(b)

FIG. 3.38

(*a*) Omegatron in vacuum system (*after Wagener and Marth*)

(*b*) Mass spectrum of residual gases recorded in the presence of a barium getter

With this omegatron, the residual gases present in a degassed kinetic all-glass system at a total pressure of $1{\cdot}5 \times 10^{-7}$ torr (as measured by a Bayard–Alpert gauge), where pumping was carried out by a mercury diffusion pump with liquid air trap, were recorded by Giorgi (Table 3.7). The omegatron was operated with an electron beam current of 2 μA, an r.f. potential of 2·1 V r.m.s. for the mass range 1 to 10 a.m.u. and 0·9 V r.m.s. for higher masses, and a trapping potential of 0·6 V.

As an example of the possibilities of this instrument in gas analysis the work of Wagener and Marth (WM1) is interesting; they used an omegatron to record the residual gases present in a vessel at a total pressure of 6×10^{-9} torr in the presence of a barium getter (§ 6.11). The gases from the gettered tube were admitted via a break seal to the pre-evacuated and degassed omegatron. The equipment used is illustrated in Fig. 3.38(*a*) and the mass spectrum, showing predominant methane, carbon monoxide and water vapour, is shown in Fig. 3.38(*b*).

Further data on gas analysis in specific cases undertaken with the omegatron are recorded in §§ 7·6 and 8·4. The use of the omegatron in leak detection practice is discussed in § 9.11.

4

VACUUM PLUMBING I: SEALS AND SEALING MATERIALS

It is convenient to distinguish between two main classes of seals: (*a*) **permanent seals** and (*b*) **demountable seals**. Under class (*a*) are included seals or joints of the following kinds: metal-to-metal, metal-to-glass, metal-to-ceramic, metal-to-plastic, glass-to-ceramic, glass-to-plastic. Class (*b*) includes seals or joints between members where the union can be dismantled and re-assembled as required; the following are concerned: the use of oils, greases, waxes and cements; unions made with tubing, gaskets and rings of elastometers such as natural, artificial and silastic rubbers and also plastics; seals made with metal rings; mercury seals. Special types of demountable seal are those in which a translatory or rotatable motion is imparted, for example, to a shaft entering a vacuum tank, and seals between the parts of isolation valves and gas-metering devices like needle valves (*see* Chapter 5).

It is not proposed to deal here with the art of making seals between glasses and glass-blowing in general. (For information on glass-blowing, *see* Barr and Anhorn, BA2; Frary, Taylor and Edwards, FTE1; Heldman, H12; Nokes, N5; Strong, S8; Breadner and Simms, BS1.)

Permanent Metal-to-Metal Seals

The methods concerned are **welding, soldering** and **brazing**. Joints made by these methods are preferred to mechanical joints with gaskets. Though a very wide variety of metals is encountered in vacuum technology, the metals commonly used for the construction of vacuum tanks, tubing, traps, baffles, bellows and vacuum valves are comparatively few in number. For large tanks (greater than 10 cu ft) steel is essential to provide the mechanical strength necessary to withstand the forces due to atmospheric pressure and temperature gradients, and stainless steel (or a steel tank with the inner walls coated with a stainless steel 'flash') is preferred. Kronberger (K7) emphasizes that plant should be constructed, where possible, from rolled plate, forgings or drawn tubing, with welding (especially argon-arc welding) as the preferred technique of joint making; castings are considered unsatisfactory for large vacuum envelopes. Smaller tanks are also often of steel but copper, aluminium and bronze are frequently used and, in some cases, where ready workability is advantageous, brass is adopted despite its porosity. Steels, stainless steels, copper and sometimes brass are also used for connection tubing between the parts of a vacuum system and for the construction of vacuum valves, baffles, traps, etc. Certain alloys must also be mentioned, such as the glass-sealing alloys, and also the stainless steels and Tombac, available in the form of flexible, corrugated tubing. Other metals encountered in specialized designs of vacuum tubes and devices where vacuum-tight seals are required are constantan, chromium, invar, molybdenum, nickel, palladium, platinum, silver, tantalum, titanium, tungsten, zirconium.

4.1. Welding Methods

The methods available are (1) oxy-acetylene welding, (2) electric resistance welding, (3) electric arc welding and (4) electron beam welding. Of these, the third is the most important in the fabrication of vacuum-tight seals between metals and, moreover, of the arc welding processes, the argon arc method is the most valuable in vacuum technology.

(1) **Oxy-acetylene welding** is a widely adopted workshop technique. Two main procedures used are *fusion welding*, in which the base metals are brought to their melting point, and *bronze welding*, in which a rod of bronze alloy is heated simultaneously with the work edges and caused to flow over these edges to form a seal. The techniques of flame-welding iron, steel, stainless steels, aluminium, copper, brasses, magnesium and bronze are fully described by Molloy (M7) and Davies (D5). The necessity for a flux, porosity of the weld, occurrence of slag and oxidation of the work reduce the applicability of oxy-acetylene welding in the manufacture of satisfactory seals for vacuum equipment, and, indeed, if a flame-heating method is used, hard-soldering (§ 4.2) is to be preferred as it is more convenient and gives better results.

(2) Two chief methods are used in **electric resistance welding**: *spot-welding*, of great value in joining wires and sheets of metals in the manufacture of electron-tube electrode structures but not applicable to making vacuum-tight joints, and *stitch welding*, in which a continuous weld is made between metal sheets overlapping by about $\frac{1}{16}$ in. and squeezed during the weld to become flush. Again, this method is only of use for thin sheet material ($< \frac{1}{8}$ in.) and is of little value in the construction of vacuum vessels, tubing, etc. Other types of resistance welding, such as seam-welding, projection welding, butt welding and flash welding are, in effect, derivations from the chief methods already mentioned. (Full details are given by Molloy, M7.)

(3) **Electric arc welding** is frequently undertaken in air and where one electrode is the work and the other the welding wire or rod (usually of the same metal as the work). D.c. or a.c. supplies may be used, but bare wire or lightly flux-coated electrodes are only deposited with difficulty if the usual a.c. plant is employed so that d.c. arc-welding is preferred for the welding of alloy or non-ferrous metals, whereas the more economical a.c. method is adopted usually for the welding of iron and steel, especially if heavily-fluxed electrodes are used. Full technical details are given by Molloy (M7) and Davies (D5).

In the construction of vacuum-tight seals between metals the electric arc method is far preferably undertaken in a shielding atmosphere of inert gas, usually argon—*i.e.* **the argon arc process**—though helium has also been used. Kronberger (K7) states that in the making of welded joints and seams in vacuum plant the argon arc process is used almost exclusively by the United Kingdom Atomic Energy Research Authority. It enables steel, stainless steel, aluminium, copper, magnesium and other metals to be fusion welded without the use of a flux; oxidation and the formation of nitrides are prevented at the weld, though oxidation of the metal surfaces is possible in zones near to the weld which become hot and are not fully shielded from atmospheric action.

The argon arc process is particularly valuable in the fabrication of large (> 100 cu ft) vacuum tanks of stainless steel. In the manufacture of smaller vacuum plant in laboratories where the argon arc apparatus is not available, hard-soldering (§ 4.2) is recommended rather than an alternative welding process.

Equipment for argon arc welding is supplied by The British Oxygen Co., Ltd. and by Knapsack-Griesheim A.G. A typical torch is shown in Fig. 4.1.

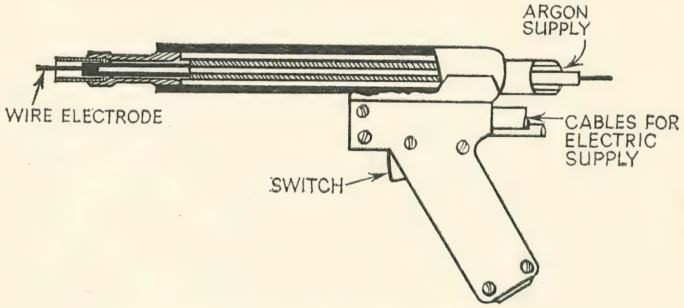


FIG. 4.1 Argon arc welding torch

Manual torches are of two sizes, one suitable for welding light sheet metals and the other for plate up to $\frac{3}{4}$ in. in thickness, whilst an automatic torch is used for thicker plate (Molloy, M7). The arc is struck between a tungsten (or special tungsten alloy containing electron-emitting materials) electrode and the work, with argon supplied from a cylinder of the gas to the ceramic shield surrounding the electrode. If a filler rod is used, the procedure is similar to oxy-acetylene welding. Small torches are air-cooled and operate at currents up to 150 amp; large torches operating at currents of as much as 300 amp (or more in automatic apparatus) are water-cooled. The tungsten electrodes range in diameter from $\frac{1}{16}$ in. to $\frac{1}{4}$ in. and can be readily interchanged. In welding aluminium and magnesium and their alloys, an a.c. supply is used, but d.c. (with the tungsten electrode negative) is preferred for stainless steel, nickel chrome alloys, copper and its alloys (Davies, D5). No flux is required, so the surfaces to be welded together must be thoroughly cleaned by a wire-brush, emery paper or file.

For satisfactory argon arc welding of stainless steel, important factors are as follows:

(*i*) The material of the welding rod has to be adapted to the type of stainless steel which may be austenitic (Cr–Ni), ferritic (containing more than 14% Cr) or martensitic (Cr). The appropriate material is supplied by the firm which distributes the argon arc welding equipment.

(*ii*) The electrode is made the cathode if d.c. welding is used.

(*iii*) Chromium-bearing stainless steels have to be heat-treated before and after welding according to a prescription laid down by the welding equipment suppliers.

(*iv*) The following must be adapted to the dimensions and shape of the work-piece: the type of nozzle; the maximum arc current; the diameter of the welding rod; the speed of welding in in. per min; the electrode diameter; the rate of supply of argon (99·9% pure) in litre per min.

(*v*) More than one welding layer is necessary for thick sheet material; *e.g.* three for $\frac{1}{2}$ in. thick sheet stainless steel.

The British Oxygen Co., Ltd. and Knapsack-Griesheim A.G. issue special booklets giving details of the many possible variations encountered in practice.

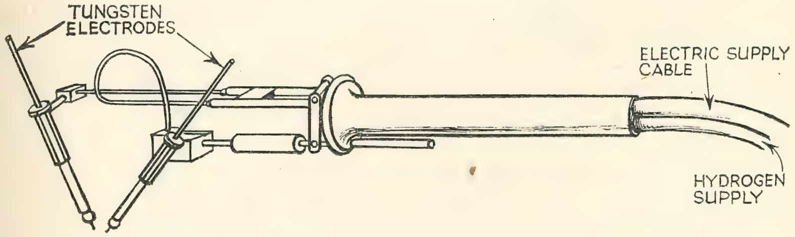


FIG. 4.2 Atomic hydrogen blow-pipe for arc-welding

In the argon arc welding of aluminium and light alloys satisfactory leak-free seals are not easily obtained. Molloy (M7) stresses that a specially designed power unit should be used in which a low-voltage high-frequency current is superimposed on the welding current to permit ready striking of the arc and the use of a longer arc.

Automatic argon arc welding plant is also marketed in which an automatically continuous wire feed is supplied to a d.c. operated torch.

Another, but less widely used, electric arc welding technique suitable for vacuum seal fabrication is the **atomic hydrogen method.** This utilizes an a.c. arc between two tungsten electrodes to which is fed a continuous stream of hydrogen. To the heat of the arc and the burning hydrogen is added the heat of recombination of the atoms of hydrogen, the molecules of which dissociate in the arc. This recombination takes place at the cooler work; temperatures as great as 4000° C are attainable. The weld is protected during fabrication by the strongly reducing hydrogen and, moreover, electrode burn-up is at a minimum since oxidation cannot occur. A blow-pipe for this process is illustrated by Fig. 4.2. Automatic plant is also marketed.

Espe (E2) lists the following combinations of metals (or alloys) which can be joined by argon arc welding: Ag–Ag; Al–Al; Cr–Cr (surfaces first cleaned with phosphoric acid); stainless steel–stainless steel; CrNi–steel; Cu–Cu; FeNi–FeNi; Kovar–Kovar; Mg–Mg; Ni–Ni; Ni–Zr; Ti–Ti; Zr–Zr (using zirconium in place of tungsten electrodes). In the same detailed table (which deals also with soldering techniques) the metals which can be joined by atomic hydrogen welding are given as: Al–Al; Co–Co; Cr–Cr; Kovar–Kovar; Mo–Mo; Ti–Ti (titanium must be subsequently freed of hydrogen by vacuum process); W–W. Other combinations than those listed by Espe are also possible.

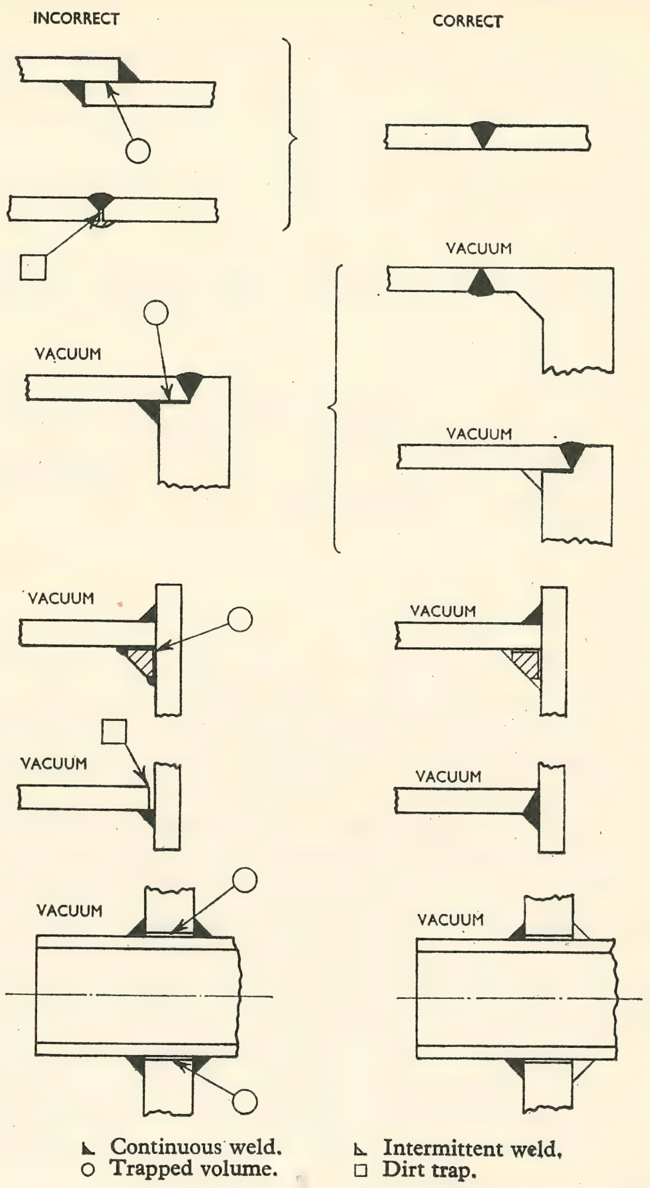


FIG. 4.3 Correct and incorrect arrangements of welds (*after Kronberger*)

In the use of any of the methods of welding for the fabrication of vacuum tanks, a one-pass weld should be made on the outside of the tank and, if a welding rod is used, it should be of sufficient length to permit this. If welds inside the tank are made, they should be discontinuous to permit pockets of gases and vapours to be pumped away.

Guthrie and Wakerling (GW1) emphasize that in the construction of large, complex vacuum plant, welding should be done so that any leaks remaining or developing may be located and repaired. Kronberger (K7) favours the argon arc welding process using filler rod and stresses that full penetration is necessary and that crevices and trapped volumes of gas should be avoided. Examples of good welding practice are illustrated in Fig. 4.3; bad practice is also shown.

(4) **Electron beam welding** is a process of considerable promise which has been developed recently by J. A. Stohr. The heat required to make the weld is produced by highly accelerated electrons from an electron gun. The electron gun is mounted above the work in a chamber within which the pressure is maintained at below 10^{-4} torr by a large capacity oil diffusion-ejector pump. Plate 4 shows the apparatus developed for this process by Edwards High Vacuum Ltd. (*Brit. Pat. Appl.* 1962/57). The work is mounted on a turntable (rotated by a drive from outside the vacuum via a rotary seal) which is at earth potential. The tungsten filament of the electron gun is at about −20 kV with respect to earth and the electrons from this filament are focused by the electrostatic or magnetic electron lens of the gun to form a small diameter spot at one point on the work where the circular weld is to be made. The maximum electron current is 100 mA and can be varied by altering the filament current whilst the spot size can be changed by altering the gun focusing. Rotation of the work beneath the stationary gun enables the weld to be carried out along the seam required, the correct location of the focused high energy electrons relative to the work being arranged by adjustment of the positions of the electron gun and/or turntable. The present Edwards apparatus enables circumferential welds on components up to 6 in. diameter to be made.

Flux is unnecessary in electron beam welding and, as the process is carried out in a high vacuum, oxidation is avoided. It is particularly useful, therefore, for welding metals which react readily with the atmosphere.

An interesting recent development is the use of a 'torch' giving a plasma 'flame' or beam consisting of totally ionized gas and able to weld or spray-coat with metals of high melting point (*U.S. Patents Nos.* 2,806,124 (1957) and 2,847,555 (1958); *see also* Pirani, P15). Temperatures of 30,000°C have been obtained.

Cold pressure welding (Steyskal, S9) can be used for soft metals such as aluminium, copper and nickel. No heating is required. At present this method is chiefly applied in vacuum technology for sealing-off from pumps the metal tubulation to an evacuated enclosure (*e.g.* a metallic thermionic tube). The copper pumping tubulation is clamped with considerable pressure between two hardened steel rollers to make a seal and to separate this pumping tube into two parts. An advantage is that no gas is released on sealing-off.

4.2. Soldering and Brazing

Methods available are **soft-soldering, hard-soldering** and **diffusion-soldering.** For heating, a soldering iron or blow-pipe is normally used, but furnace soldering and brazing and the use of high-frequency eddy-current heating are valuable procedures in the construction of vacuum apparatus, especially as

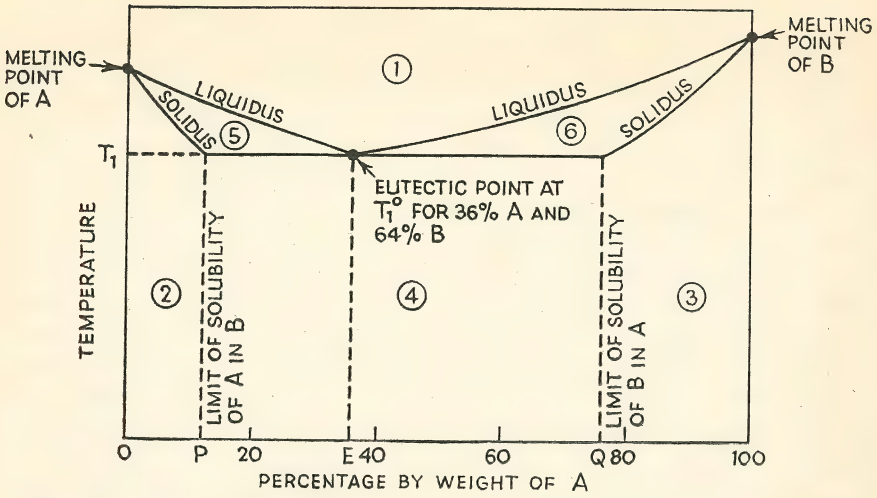

MELTING POINT OF A
MELTING POINT OF B
①
LIQUIDUS
SOLIDUS
⑤
LIQUIDUS
⑥
SOLIDUS
T_1
EUTECTIC POINT AT T_1° FOR 36% A AND 64% B
TEMPERATURE
②
LIMIT OF SOLUBILITY OF A IN B
④
LIMIT OF SOLUBILITY OF B IN A
③
0
P
20
E 40
60
Q 80
100
PERCENTAGE BY WEIGHT OF A

FIG. 4.4 Equilibrium diagram for an alloy of metal *A* with metal *B* where the percentage by weight of *A* varies from 0 to 100, showing the effect of a change of temperature from the higher melting point of *B* down to 0° C

they can be carried out in an atmosphere of hydrogen, of an inert gas or in a vacuum.

Most solders are alloys of two or more metals, though pure metals are also used. If, in an alloy, two metals (or more) are partially soluble in each other in the solid state but do not form compounds, they have a particular *eutectic composition*. Consider such an alloy of metals *A* and *B* (Fig. 4.4). The regions denoted by numbers on this chart are as follows:

(1) Single-phase liquid solution of *A* and *B*.
(2) Single-phase solid solution of *A* and *B*.
(3) Single-phase solid solution of *B* and *A*.
(4) Two-phase mechanical mixture of the solid solutions of (2) and (3).
(5) Two-phase mixture of liquid solution of *A* and *B* with solid solution of *A* and *B*.
(6) Two-phase mixture of liquid solution of *A* and *B* with solid solution of *B* and *A*.

If the alloy contains less than *P*% of *A* (*see* Fig. 4.4) solid crystals will begin to separate out as it cools from the molten state. The liquid will change in composition along the liquidus curve whereas the solid will change along the solidus curve. For slow cooling, the eventual solid solution formed will be of phase (2). This means that not only will there be a change of composition of the alloy during cooling but also that there is no definite melting point. There will be, in fact, an upper temperature on the liquidus curve at which solidification first starts and also a final solidification point T_1. A similar state of affairs exists for an alloy with originally more than *Q*% of *A*. Alloys with a percentage of *A* between *P* and *Q*, but not having the eutectic composition *E*, will again have an upper solidification temperature and a lower solidification

temperature at T_1, and they will begin to solidify on cooling from the molten state as a solution until the liquid composition reaches the eutectic value when the remainder will solidify as an eutectic alloy. It is only the eutectic alloy proper with *E*% of *A* that has a definite solidification point equal to the melting point at which constant temperature crystals of the two solid solutions will separate out simultaneously in the form of an alloy of fine mechanical mixture.

Steyskal (S9) points out that if, for example, pure silver (melting point 960·8° C) were used as a solder on copper (melting point 1083° C) as the base metal, relatively large amounts of copper would dissolve in the silver; a thin copper base would therefore become distorted and, on cooling, crystals rich in copper would be deposited. If, however, the eutectic Ag–Cu alloy (Cu 28%; Ag 72%) were used, it would be necessary to exceed its melting point (779° C) by only about 30° C for 5 min, say, and during solidification the change of composition due to diffusion of copper from the base metal would be negligible.

Soft solders have flow points at temperatures less than 400° C. In general, they are therefore unsatisfactory for making joints in parts of vacuum plant which have to be degassed by baking. They are, however, often used for joining metal parts in continuously-pumped kinetic vacuum systems and for junctions in the tubulation on the backing side of vacuum plant in general.

A class of soft solders is the tin solders which are composed primarily of tin and lead, though as much as 0·1% of iron and 0·2% of copper plus arsenic and nickel may be present as impurities (*see* Table 4.1).

TABLE 4.1
The Sn–Pb soft solders

Composition		Melting point		Remarks
Sn	Pb	Upper	Lower	
		°C	°C	
100		232	232	Pure tin; attractive because vapour pressure is low
63	37	183	183	Eutectic; highest tensile strength
60	40	190	183	
50	50	212	183	Generally used 50/50 solder
40	60	238	183	Most ductile
30	70	257	183	Plumbers' solder: best for withstanding tension and compression
5	95	313	290	Usable up to 210° C
	100	327	327	Pure lead

The fluxes used for these tin solders are (*a*) liquid solution comprising 40% ZnCl, 20% NH_4Cl, 40% H_2O, (*b*) a paste of 10% NH_4Cl in petroleum jelly; (*c*) a solution of resin in alcohol. For electrical application where a non-corrosive flux is essential, (*c*) is preferred. (*a*) is chiefly used with a gas blow-pipe flame of reducing character. Fluxes for various purposes are available commercially, also a solder containing a flux-filled (resinous) core. Tallow is usually employed for soldering lead. Flux residue must be removed from soldered parts to be exposed to vacuum: acidic fluxes are best washed in warm water containing soda or lime and then rinsed with distilled water and finally methyl alcohol.

Other soft solders are: **Wood's metal** (Bi 50, Pb 25, Sn 12·5, Cd 12·5) which has a melting point of 65·5° C and is valuable when only slight heating can be tolerated, *e.g.* in the neighbourhood of glass or for soldered joints to silvered glass, but the joint is weak; **Sb 50, Pb 25, Cd 5,** which flows at 150° C and is recommended for Ag–Cu joints, especially in joining tinned copper wires to silvered glass; **Cd 78·4, Zn 16·6, Ag 5,** which flows at 280° C and is suitable for joints between Cu and W. However, solders containing cadmium are not recommended for use in vacuum because this metal has a high vapour pressure at elevated temperatures.

The soft silver solders have two advantages over the Sn–Pb solders: they offer much greater resistance to creep under load and they can be readily galvanized. Examples are eutectic **Pb 94, Ag 6** with a melting point of 304° C and eutectic **Sn 89, Ag 11** which melts at 221° C and is recommended for joining copper to molybdenum. *See also* Table 4.2.

TABLE 4.2
Soft silver solders
(Johnson, Matthey and Co., Ltd.)

Alloy	Com-position	Melting range in °C	Tensile strength ton/sq in.	Remarks
Comsol	Ag–Sn–Pb	296	2·5	Very low solvent action on copper
A5	Ag–Pb	304–370	2·5	For installations handling hard water
Plumbsol	Ag–Sn	221–225	1·7	For installations handling soft water
LM10A	Ag–Sn	214–275	4·8	
LM15	Ag–Cd–Zn	280–320	11·5	Note high strength (compare Sn 63, Pb 37 with 3·4 ton/sq in.)
LM5	Ag–Cd	338–390	8·4	

Soft silver solders
('Thessco': The Sheffield Smelting Co., Ltd.)

Grade	Melting range °C		Remarks
	Liquidus	Solidus	
SX4	224	221	Resists water corrosion; lead-free
SX5	285	270	Very strong and corrosion resistant
SX10	300	221	Lead-free
SX25	305	320	Tin-free
SX75	365	275	Very strong and corrosion resistant

The usual soft solder fluxes are used for soft silver solders. Soft solders are supplied in the form of wire (usually $\frac{1}{8}$ in. dia), ingots and as washers, rings and other shapes for insertion as pre-placements in furnace-heated assemblies, *e.g.* using gas or electric resistance heating or h.f. induction heating.

Solder paints are supplied by a number of firms. These are usually powdered tin–lead solders (available in special compositions for specific purposes to any British Standard specification) combined with flux in the form of semi-liquid paste or 'paint' and applied to the heated metal. Epatam 3311 (Perdeck Solder Products Ltd.) solder paint can be used to tin practically all metals except aluminium and its alloys. Fryolux solder paint (melting point liquidus 234° C) is a similar material available from Fry's Metal Foundries Ltd. Other solder paints from these firms are listed in Table 4.3.

TABLE 4.3
Solder paints
(Perdeck Solder Products Ltd.)

HD830: high density of restricted flow properties for gap filling.
PLF/23/04: for tinning cast-iron.
NSPI: non-spattering for H.F. induction heating.
Tinning salt 'Epatam 3311' for tinning rusty or grimy surfaces.
'Kolosol': non-corrosive for tinning copper or brass.
Pure tin paint 'Epatam 3311' for tinning and soldering food containers.

(Fry's Metal Foundries Ltd.)

Grade	Melting point °C (liquidus)	Applications
Fryolux K	190°	Low temperature general soldering and tinning
Fryolux pure tin	232°	Lead-free
Fryolux 298	320°	
Fryolux No. 2	234°	For work to be electroplated after soldering
Fryolux W.B.	191°	Work requiring high lustre finish
Fryolux A20: for cast iron and aluminium (heat to 320° C)		

Copper, brass, tin and lead can all be soft-soldered readily; eutectic **Sn 64, Pb 36** is recommended for Ag–Ag, Ag–Cu, Cu–Cu, and Cu–Kovar; alternatively a soft silver solder like 'Comsol' or LM15 (Table 4.2) if particularly high strength and creep resistance are necessary. Cast iron cannot easily be tinned unless it is previously etched, filed, rubbed with emery paper, or sand-blasted; tinning is facilitated, however, if a solder paint like Epatam PLF/23/04 or Fryolux A20 is used. Tungsten, molybdenum and tantalum cannot be soft-soldered unless they are first plated with copper; platinum and gold can be soft-soldered, but the joint is brittle unless the time of heating is short and the increase of temperature is restricted by the use of a solder with a low flow temperature. It is not possible to soft-solder magnesium. Soft-soldered joints are not desirable within high vacuum but if so used should preferably be coated with a pure tin (or use pure tin solder, *e.g.* for Cu–Cu) which has a very low vapour pressure (10^{-5} torr at 823° C).

Soft-soldering of aluminium can be undertaken, but special methods are necessary to break down the troublesome refractory oxide film. Soft soldered joints in aluminium are, moreover, susceptible to corrosion on exposure to moisture. This oxide film is removed during the initial tinning process either by abrasion or friction or by ultrasonic vibrations. Soft solders for aluminium are **Sn 90, Zn 10** (melting range: 200–210° C), **Sn 80, Zn 20** (melting range: 199–267° C) and **Sn 86, Cd 6, Sb 6, Cu 2** (melting at 250 ±5° C), but only the last of these has good corrosion resistance, and the proprietary solders listed below are much preferred. A solder paint consisting of a pulverized suspension of tin or tin alloy in flux applied at 280° C is suitable. The usual resin and paste fluxes are only suitable for aluminium when used in conjunction with some abrasion method, *e.g.* rub soft solder into heated aluminium with a wire brush. It is much better, however, to use a special flux of which two main types are organic and reaction fluxes. A useful organic flux is triethanolamine acting as a vehicle for ammonium fluoride, ammonium hydrogen fluoride or ammonium fluoborate, and applied at 215–270° C. The reaction fluxes are generally mixtures of fluorides and chlorides and are more efficient, but require a higher operating temperature. The proprietary fluxes of both kinds usually contain easily dissociated salts of Pb, Sn, Cd or Zn so that thin films of these metals are deposited on the work and wetting by the solder is facilitated.

Proprietary soft solders suitable for aluminium (other than for electric cable work) are (*Aluminium Development Association Information Bulletin* 23): Enthoven AS10, AS20 (Enthoven Solders Ltd.); Amalgam AL 1, 2 and 3 (Grey and Marten Ltd.); TL Solder 1P (Tiltman Langley Ltd.); Fry's LM, Fryal (Fry's Metal Foundries Ltd.) and Epatam A66, A67 (Perdeck Solder Products Ltd.). Epatam 3311, Mark 1 (Perdeck Solder Products Ltd.) and Fryolux A20 (Fry's Metal Foundries Ltd.) are suitable solder paints. Proprietary fluxes for soft soldering aluminium are Kynal (zinc in organic base; 280° C; I.C.I. Metals Division and Fry's Metal Foundries Ltd.); Enthoven (organic base in liquid or paste form; also available as flux-cored solder; 300° C; Enthoven Solders Ltd.).

The solder should be heated directly in contact with the work surface, and heating rapidly to the working temperature of the solder is essential. If the work can be pre-heated on an electric hot-plate, soldering is facilitated. Abrasion soldering of aluminium may be undertaken even without flux, using a wire brush or a specially electrically-heated soldering iron incorporating a steel wire brush which is vibrated vertically at 100 times per sec (The Belark Tool and Stamping Co., Ltd.). A glass-fibre brush, without heating device, with which the oxide film can be abraded beneath a molten pool of solder is supplied by Tiltman Langley Ltd. The best way of soldering aluminium is, however, to use ultrasonic disruption of the oxide film. A transducer producing ultrasonic vibrations at 20–25 kc/s (Mullard Ltd.) produces small gaseous pockets within the molten solder which disrupt the oxide film on the surface of the aluminium. An ultrasonic transducer with a built-on gas torch is commercially available.

The flux residues should be removed after soldering by very hot water (if inorganic) or industrial spirit or trichlorethylene (if organic). Another recommended procedure (Aluminium Development Association) is to immerse the soldered article in 5 to 10% NaOH, water rinse, neutralize by dipping in 2% phosphoric acid, wash in water and then dry.

Aluminium alloys containing more than 1% magnesium or silicon cannot be soldered at all readily. Aluminium can be soldered to steel, brass or copper if both surfaces are first tinned with, *e.g.* **Sn 80, Zn 20** solder. It is difficult to soft solder aluminium to stainless steel; hard silver solders are preferred. Aluminium bronze (copper alloy containing about 10% Al) can be soldered if the special flux Frysol S26 (Fry's Metal Foundries Ltd.) is used; Fry's LM solder is recommended for strength.

It is desirable to protect soldered joints in aluminium against the action of atmospheric moisture by painting or binding with a waterproof tape. In vacuum technology, this susceptibility to moisture often means that welding must be used and not soldering in the case of aluminium.

All the **stainless steels** can be soft-soldered. Polished surfaces must be roughened by filing, emery paper, etching in a mixture of 2 parts HCl with 1 part HNO_3, or sand-blasting. Resinous fluxes are not satisfactory. Commercially available acidic fluxes containing zinc chloride with free hydrochloric acid are used, alternatively, concentrated phosphoric acid.

Hard solders may be classified as **silver-solders**, of which a wide range of alloys exist with melting points above 400° C, **brazing alloys, special alloys** and **pure metals** such as silver, copper and gold. Brazing, as distinct from hard soldering, is defined (British Standard B.S.499: 1952) as 'the process of joining metals in which molten filler metal is drawn by capillary attraction into the space between closely adjacent surfaces of the parts to be joined'. In general, the melting point of the filler metal is greater than 500° C. In most brazing, copper–zinc alloys, *i.e.* 'brasses', are used—hence the term.

Compositions of some hard silver solders are given in Table 4.4.

TABLE 4.4
Hard silver solders

Composition % by weight	Melting point °C		Remarks
	Liquidus	Solidus	
Ag 20, Cu 3, Zn 2, Sn 75	400		Intermediate solder between soft and hard (Strong, S8)
Ag 5, Zn 95	450	420	For aluminium, copper and iron
Ag 45, Cu 35, Sn 25	630	600	Hard, brittle
Ag 50, Cu 15·5, Zn 16·5, Cd 18	636	620	'Easy-flo'; strong
Ag 15, Cu 80, P 5	704	641	'Sil-fos'; for non-ferrous metals
Ag 63, Cu 27, In 10	710	685	Used particularly for electron tubes
Ag 72, Cu 28	778	778	Eutectic; best for copper

Hard silver solders are supplied by several firms; examples are given in Tables 4.5, 4.6 and 4.7.

These silver solders are available in form of rod, wire, cut strip and foil. Except for silbralloy, pre-placement rings, washers, discs and special shapes are available for furnace soldering. Easy-flo No. 3 is supplied also as a paste preparation known as Easy-flo paint and consists of a finely divided mixture of Easy-flo metal powder, Easy-flo flux and a volatile liquid medium. It can be applied satisfactorily to mild, carbon and alloy steels, nickel and nickel-base alloys and all copper-base alloys except those containing more than 2%

TABLE 4.5
Hard silver solders
(Johnson, Matthey and Co., Ltd.)
BS1845 is a British Standard Specification

Name	Melting range °C	Flux used	Remarks
Argo-flo (DTD 900: 4043)	605–651	Easy-flo	Quaternary alloy; long plastic range
Argo-swift	607–700	,,	Similar to Argo-flo but lower silver content
Easy-flo No. 2 (DTD 900: 4117)	608–617	,,	Lowest silver content consistent with low, short melting range for wide range of dissimilar metals
Argo-bond	616–735	,,	Very long plastic range
Easy-flo (Type 3, BS1845)	620–630	,,	Eutectic type alloy with max ductility and ability to join dissimilar metals
Sil-fos (Type 6, BS1845)	625–780	None for Cu; Tenacity flux 4A	Unsuitable for steel or nickel alloys. Highly recommended for copper and its alloys, especially for furnace soldering in protective atmosphere
Easy-flo No. 3	634–656	Easy-flo	For steels which are difficult to wet; special alloy for tungsten carbide tool dipping
Silbralloy	638–694	None for Cu; Tenacity flux 4A	Unsuitable for steel or nickel alloys. Flux-free brazing of copper at low cost
Type 4, BS1845	690–737	,, ,,	For high conductivity. High silver, low zinc content; particularly used in reducing atmosphere without flux
Type 5, BS1845	698–788	,, ,,	Long plastic range
D 3	700–740	,, ,,	Popular for both ferrous and non-ferrous work
G 6	705–723	Easy-flo	For hall-marked silver ware
C 4	740–780	Tenacity flux 4A	All metals, especially for two-stage soldering in conjunction with Easy-flo
Eutectic	778	Tenacity flux 4A	Silver–copper eutectic; excellent for copper in vacuum tube joints and for use without flux in hydrogen furnace
B 6	790–830	,, ,,	For high temperatures

aluminium, but is unsuitable for cast iron, aluminium and zinc alloys. It can be thinned with methylated spirits.

The Sheffield Smelting Co., Ltd. range of 'Thessco' silver solders is given in Tables 4.6 and 4.7.

Of these silver solders, those most commonly used are Easy-flo No. 2 (Table 4.5) or the similar MELT-ES1 No. 2 MX12 (Table 4.6) and Sil-fos (Table 4.5). Easy-flo No. 2 is outstandingly fluid and penetrative and is effective in the widest possible range of metals, *e.g.* austenitic stainless steels; mild, carbon and alloy steels; copper; brass; gun-metal; tin bronzes; aluminium and manganese bronzes; copper–nickel alloys; and nickel brasses of all types. Sil-fos is especially suitable for copper and copper alloys containing only a small percentage of the alloying element, as it can be used on the clean metal without flux to provide a joint of great mechanical strength. For brass and bronze, Tenacity flux 4A is used, unless soldering is undertaken in a reducing atmosphere.

TABLE 4.6
Hard silver solders
(The Sheffield Smelting Co., Ltd.)

Grade	Melting range °C		Flux	Remarks
	Solidus	Liquidus		
MXO	605	680	C or Y	Especially for steel; usable on practically all ferrous and non-ferrous alloys
MX8	606	648	,,	For wide range of metals and alloys
MELT-ES1 No. 2 MX12	608	621	,,	For wide range of ferrous and non-ferrous metals and alloys, including stainless steel
MELT-ES1 MX18	630	640	,,	Like MX12 but greater ductility and strength
MELT-ES1 PLUS	640	660	,,	Wets tungsten carbide
M1	714	755	B or X	Strong, especially for brasses and bronze, also ferrous alloys
LX13	718	773	,,	For practically all metals
Super melt ES1	735	814	,,	Specially for stainless steel and many non-ferrous alloys
LX7	810	835	,,	Very strong, particularly suitable for brass
Silbraze	886	893	B or No. 5	Ductile; great strength; specially suitable for copper and high copper alloys

Fluxes for hard silver soldering. Borax or paste of 10 parts borax with 1 part boric acid is used for silver soldering, but it has a rather high melting point and sometimes insufficient cleaning ability compared with the proprietary fluxes, which are usually preferred. Thus borax is unsuitable for Easy-flo No. 2 solder (melting range 608–617° C) and Easy-flo flux is preferred. This flux is of the fluoride type, is fully fluid and active at 650° C and is able to dissolve rapidly a wide range of metallic oxides. For soldering stainless steel with Easy-flo solders, a flux known as Easy-flo stainless steel grade should be used, whilst Easy-flo flux aluminium bronze grade is available for bronzes of aluminium content greater than 2%. For soldering at temperatures in excess of 750° C up to 1000° C, Tenacity flux 4A should be used. The 'Thessco' fluxes supplied by the Sheffield Smelting Co., Ltd. are all in the form of white powders which are mixed to a paste with water. They are designated as B (temperature range: 700–1000° C), C (450–750° C), X (650–1000° C), Y (550–750° C, especially suitable for high frequency brazing as flux bubbling is slight), Z (450–1000° C, especially designed for silver-soldering aluminium bronze), No. 5 (700–1000° C, suitable where great flux penetration is required and no pre-placed parts might be displaced by bubbling).

TABLE 4.7
Special hard solders for selected uses
(The Sheffield Smelting Co., Ltd.)

Grade	Melting range °C		Flux	Remarks
	Solidus	Liquidus		
H	674	677	C or Y	For stainless steels
M8	678	775	B or X	General use on nearly all metals
H10	778	782	B or X	Very high electrical conductivity. No flux in protective atmosphere furnace
L3	840	855	B or X	To withstand high temperatures
Phosphalloy No. 2	690	835	None for Cu, otherwise B	Very wide plastic range; specially for copper (no flux). Not to be used on steels
British Standard 1845: 1952				
4 (Grade 'A')	720	746	B	High electrical conductivity
5 (Grade 'B')	690	780	B	
3 (Grade 'C')	635	645	C	Suitable for nearly all ferrous and non-ferrous metals
6 (Phosphalloy)	645	780	None for Cu, otherwise B or X	Especially for Cu. Not for steels

As these fluxes are typically a mixture of KCl, LiCl and NaF, they are hygroscopic and accelerate corrosion. Residues must therefore be removed by washing in warm water or warm 5% H_2SO_4.

Suitable designs of hard-soldered joints are shown in Fig. 4.5.

Special alloys and some **pure metals** for hard soldering are listed in Table 4.8.

The usual **brazing alloy** for steels, cast-iron and copper is **Cu 54, Zn 46** which melts at 875° C and is used with borax flux. Angerer (A3) recommends **Cu 42, Zn 46 (min)** melting at 845° C for nickel and copper. The brazing of aluminium and its alloys (*Aluminium Development Association*) makes use of a brazing material in the form of an aluminium alloy having a melting point lower than that of the parent metal. Flame-brazing (in which a filler rod of the brazing alloy is pre-fluxed so that it will melt and flow into the joint) and flux-dip brazing (in which the brazing alloy is a pre-placement part on the assembly which is pre-heated and dipped into a bath of molten flux at a temperature above the melting point of the brazing alloy) are both used. Furnace brazing is also employed (§ 4.3), but a protective atmosphere is of no advantage with aluminium. The aluminium alloys suitable for brazing are listed in Table 4.9.

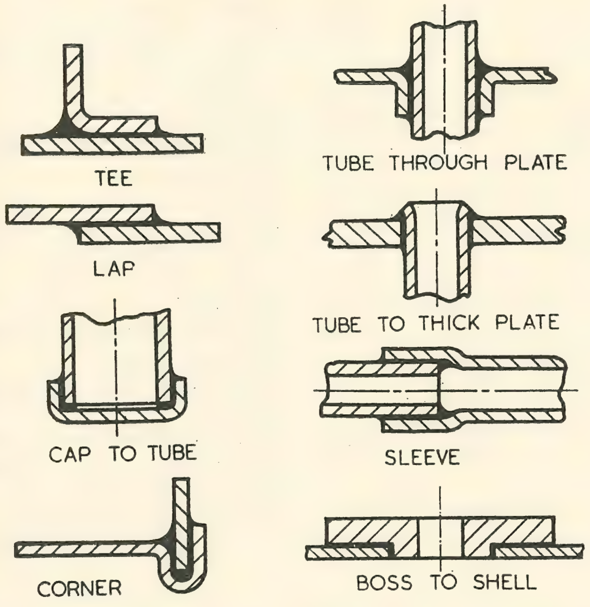


FIG. 4.5 Correct arrangements of soldered joints
(*Johnson, Matthey and Co., Ltd.*)

The best flux is a proprietary type consisting of a mixture of chlorides and fluorides like Easy-flo. The surfaces of the aluminium must be extremely clean. A flux containing not more than 8% by weight of zinc chloride is necessary to ensure wetting if the aluminium surface is other than lightly oxidized. For furnace or flux-dip brazing, the aluminium surfaces should be first degreased (*e.g.* with trichlorethylene) and then chemically etched with a solution in water of 2% by weight caustic soda with 5% by weight sodium silicate at a temperature of 90° C; alternatively, etching can be carried out by

TABLE 4.8

Special alloys and pure metals for hard-soldering

Composition % by weight	Melting point °C		Remarks
	Liquidus	Solidus	
Au 80, In 20	632	550	Hard, brittle
Au 93, P 7	750	707	Self-fluxing for non-ferrous metals (Westinghouse)
Au 80, Cu 20	890	890	Eutectic, brittle; borax flux
Au 82·5, Ni 17·5	950	950	Eutectic, wets tungsten, strongly recommended for electron tubes (Steyskal, S9), borax flux
Au 94, Cu 6	980	950	Borax flux
Au 37·5, Cu 62·5	990	950	Strongly recommended by Steyskal (S9), borax flux
Au 35, Cu 65	1010	970	Borax flux
Cu 75, Ni 25	1205	1205	Eutectic; excellent for tungsten
Ni 53·5, Mo 46·5	1320	1320	Eutectic; for molybdenum
Pure metals			
Ag	960·8		Borax flux
Au	1063		Borax flux: *see* diffusion-soldering (§ 4.4)
Cu	1083		Very good for iron
Ni	1450		Wets tungsten and molybdenum; useful for iron
Zr	1860		Wets tungsten and molybdenum
Rh	1966		For joining tungsten and molybdenum (Steyskal, S9)
Nb	2500		For tantalum (Steyskal, S9)

TABLE 4.9

Aluminium filler alloys for brazing

(*The Aluminium Development Association Ltd.*)

Type	Composition			Melting range °C	Brazing range °C
	Al	Cu	Si		
B.S.1942 (1953)					
1	Rem.[1]	2–5	10–13	550–570	570–640
2	Rem.	—	10–13	565–575	585–640
3	Rem.	—	7–8	565–600	605–615
4	Rem.	—	4·5–6·5	565–625	620–640

[1] Remainder

using hydrofluoric acid (1% by vol. in water) at room temperature. Subsequently, the parts must be thoroughly washed and dried and, if caustic soda etching is used, also neutralized by dipping in 15% HNO_3 followed by a rinse in warm water.

4.3. Furnace Brazing and Soldering

Soldering and brazing are often most conveniently carried out in a furnace which is heated by gas or electricity or where high frequency induction heating is used. Apart from convenience for assemblies which can be suitably mounted and where pre-placement solder rings, clip-rings, washers or other solder shapes are placed in position, the heating of the parts to a uniform temperature in a furnace (as compared with the use of a flame) relieves stress. Of particular value in vacuum technology, and especially for hard-soldering, it is preferable to dispense with a flux and make the soldered joint in an atmosphere of hydrogen which, being strongly reducing, ensures a clean union. As alternatives to hydrogen, a mixture of 80% nitrogen with 20% hydrogen may be used or the joint may be soldered in a vacuum furnace.

A **hydrogen furnace** usually has the form of a ceramic tube surrounded by an electrically heated winding with a supply from a cylinder of the gas to this tube of hydrogen which is ignited. For smaller parts, **bottle brazing** may be used in which case the work is heated by radiation from a tungsten or molybdenum coil within a heat shield, the whole being within a Pyrex bell-jar to which a trickle of hydrogen is supplied (Fig. 4.6(*a*)). Induction heating may be used in which a coil carrying h.f. alternating current is arranged outside a Pyrex, silica or ceramic tube which is filled with hydrogen or evacuated (Fig. 4.6(*b*)). This method of high-frequency brazing is especially convenient when it is required to localize the heat to the immediate vicinity of the joint to be soldered (Yarwood, Y4).

The surfaces to be soldered in hydrogen or in vacuum must be first degreased and chemically cleaned and should not be handled before insertion. The parts have to be arranged in jigs or clamps so that the surfaces to be joined are held firmly together with the pre-placement solder shape in position, allowing for differential thermal expansion, if it should occur. The arrangement should be such that the action of gravity and/or surface tension on the molten solder does not cause the solder to creep undesirably into cracks in or over surfaces of the work. No flux is used. Jigs and clamps are best made of chromium-bearing stainless steel and are pre-heated in hydrogen to produce a protective coating of chromium oxide (*M.I.T. Tube Laboratory Manual*, 1951) to which solder will not adhere. The use of stainless steel jigs can, however, be avoided by careful arrangement so that solder does not reach the jig. Silver from silver-solders may also be prevented from flowing over surfaces by coating with aluminium oxide in a nitrocellulose binder (*M.I.T. Tube Laboratory Manual*, 1951) which burns off during heating.

Hydrogen brazing and soldering of copper, steels not containing chromium, nickel and nickel alloys (without chromium or aluminium), Kovar, silver, tungsten and molybdenum and other metals and alloys is readily performed if the correct solder is chosen. The eutectic **Ag 72, Cu 28** solder (*see* Table 4.4) is most frequently used. Solders with volatile constituents (lead, zinc, cadmium) are undesirable. OFHC (oxygen-free, high conductivity) copper is preferred to ordinary electrolytic copper for fabricating the parts to be soldered because the latter contains oxides which produce water in the hydrogen stove leading, on production of steam, to porosity and even fractures in the metal. Beryllium-copper should be plated with nickel or copper before soldering. Brass and other zinc-bearing alloys are best brazed in hydrogen in an apparatus reserved for this purpose and where the volatilized zinc can be removed from the surfaces of the furnace when required. The bottle-brazing apparatus is preferred as it is readily dismantled for cleaning.

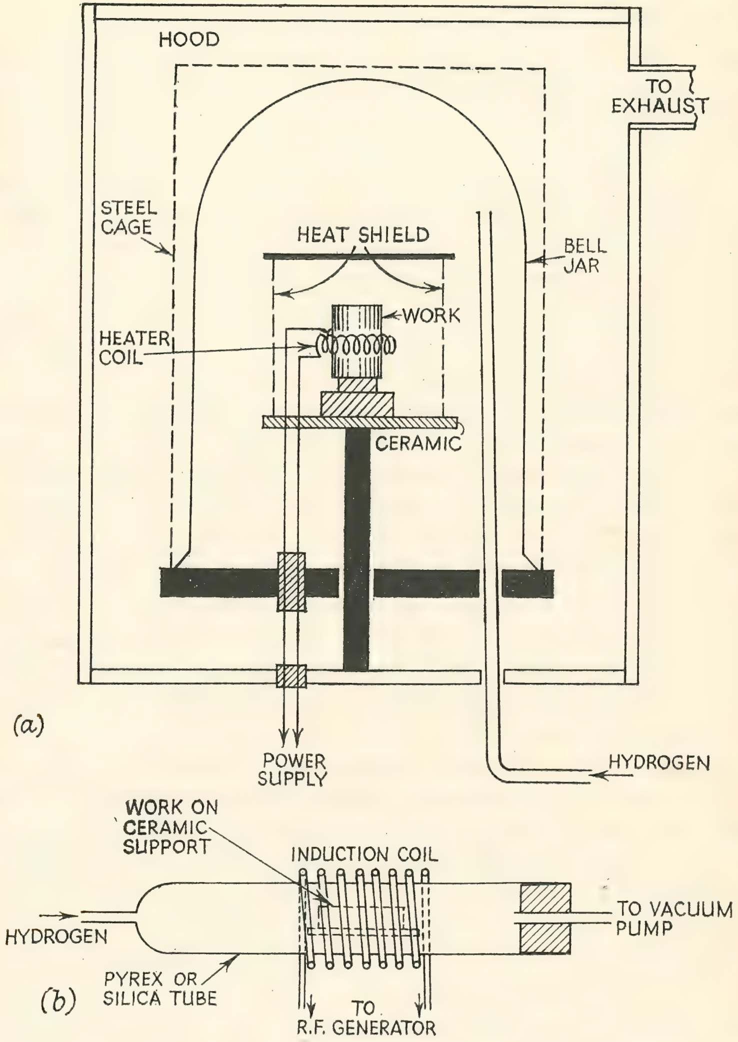


FIG. 4.6

(*a*) Hydrogen-brazing under a bell-jar (bottle brazing)
(*b*) Brazing or soldering by high-frequency induction heating

Hydrogen brazing with silver as the solder previously electroplated to a thickness of at least 30 micron on closely-fitting plane copper surfaces to be joined is a successful and useful technique. Copper or the gold–copper and gold–nickel alloy solders (Table 4.8) are preferred for Kovar to Kovar, steel or nickel (*M.I.T. Tube Laboratory Manual*). If the eutectic alloy **Ag 72, Cu 28** is employed, Kovar should be pre-heated to 850° C or more to relieve stress and then copper-plated.

Recommended hard solders for particular pairs of metals are given in the following list (*see also* Espe, E2).

Eutectic **Ag 72, Cu 28** at 779° C, preferably in hydrogen atmosphere for Ag–Ag, Ag–CrNi, Ag–Cu, Ag–FeNi, Ag–Ni, Au–Au (no flux required even if flame heated), Be–Cu (use short period h.f. heating; preferably solder Be to Fe with pure copper and then Ag, Cu solder between Fe and Cu at about 830° C), Be–nickel and nickel alloys, Cu–Cu, Cu–Fe (copper-plate Fe first and sinter in hydrogen), Cu–FeNi, Cu–nickel and nickel alloys, Cu–W (etch W first in mixture of 1 part by vol. conc. HNO_3 with 1 part conc. HF, then wash in distilled water and methyl alcohol), FeNi–FeNi (best copper-plate first to avoid intergranular penetration), Kovar–Kovar (h.f. heating in hydrogen for 5 min max and cool slowly), Kovar–Monel (h.f. heating in vacuum), Ni–Ni. For Cu–Kovar, copper-plate Kovar first and sinter in hydrogen for 30 min at 900° C, then solder quickly.

Ag 50, Cu 50 at 870° C for Be–Monel (h.f. heating in vacuum), CrFe–Cu (for rods, spot-weld Ni to CrFe, then solder Ni to Cu), Cu–Cu, Cu–FeNi, Cu–Ni, Kovar–Monel (h.f. heating in vacuum), Ni–Ni.

Pure silver at 960° C for CrNi steels to Kovar (heat for 15 min max in hydrogen), Cu–Kovar (for massive copper pieces only and short heating times), Fe–Fe, Fe–Kovar (15 min max in hydrogen), Kovar–Mo, Ni–Ni, Ti–Ti (in vacuum or use flux containing AgCe and acetylene flame). For Cu–W, first nickel plate tungsten.

Ag 85, Zr 15 for CrFe–CrFe (in nitrogen or vacuum) and CrNi–steel to CrNi–steel (in nitrogen or vacuum).

Ag 50, Cd 18, Zn 16·5, Cu 15·5 ('Easyflo' solder) at 636° C for CrNi–Cu (Cd and Zn volatilize readily on heating in vacuum).

Ag 73, Pt 27 at 1185° C for W–W.

Eutectic **Au 80, Cu 20** at 883° C for Ag–Ag, Cu–W.

Au 81·5, Cu 18·5 at 880° C for Cu–Cu, Cu–FeNi, Fe–Fe, Kovar–Kovar, Kovar–W (5 min heating in hydrogen at 920° C).

Au 42, Cu 55, Ag 3 at 950° C for Cu–Cu and Fe–Fe.

Au 75, Cu 20, Ag 5 at 990° C for Cu–Cu and Fe–Fe.

Au 58, Cu 40, Ag 2 at 935° C for Fe–Fe.

Eutectic **Au 82·5, Ni 17·5** at 950° C for Mo–Mo, Mo–W and W–W.

Pure gold at 1063° C for CrNi steels to Kovar, Fe–Kovar, Pd–Pt (with flame) and for diffusion-soldering (*see* § 4.4).

Pure copper at 1084° C for Be–Fe (h.f. heating in hydrogen), CrFe–CrFe,

CrFe–Fe (in vacuum), CrNi steel to Kovar, Fe–Fe, FeNi–FeNi, Kovar–Kovar, Kovar–Monel, Kovar–Ni (best h.f. heating), Mo–Mo (Mo rods to sheet with borax flux; bottle brazed in 80% N_2, 20% H_2), Monel–W, Ni–Ni, Ta–Ta (in vacuum).

Cu 97, Si 3 at 1025° C for Cu–Cu.

Cu 70, Au 30 at 1010° C for Cu–Cu, Fe–Fe and Kovar–Kovar.

Cu 91·6, P 8·4 at 714° C for Cu–Cu (flows well without flux but on heating phosphorus has high vapour pressure).

Cu 80, Ag 15, P 5 at 640 to 704° C for Cu–Cu (phosphorus has high vapour pressure, but useful for soldering copper to copper of copper-glass seals; Espe (E2) recommends soldering with short electric current between carbon electrodes). Also for Cu–Kovar, but Kovar must be previously copper-plated.

Cu 55, Au 42, Ag 3 at 950° C for Cu–Kovar and Fe–Fe.

Cu 80, Au 20 at 890° C for Cu–Kovar.

Cu 55, Ni 45 (*i.e.* constantan or eureka) at 1300° C for Fe–Kovar, Mo–Mo, Mo–W, W–W.

Cu 75, Ni 25 at 1205° C for Fe–Kovar, Mo–Mo, Mo–W, W–W.

Pure nickel at 1450° C for Fe–Fe.

Eutectic **Mo 46·5, Ni 53·5** at 1320° C for Fe–Fe.

Eutectic **Ni 53·5, Mo 46·5** at 1320° C for Mo–Mo.

4.4. Diffusion-soldering

A technique which has been of value in the construction of specialized types of electron tube such as magnetrons is that of diffusion-soldering. The solder is not melted but heated so that it diffuses in the solid phase. Intimate contact between the parts to be joined and the solder is necessary. An example is the use of soft gold wire (usually of about 0·5 mm dia) as the 'solder' in the form of a ring between flat copper flanges. The gold ring is compressed between the flanges in a screw clamp and is then heated to 400–450° C for about 15 min, preferably in an atmosphere of inert gas. The inter-diffusion of gold and copper produces a quite robust vacuum-tight seal. If iron flanges or other flat surfaces are to be diffusion-soldered in this way, the iron surfaces must first be plated with copper to a thickness of about 0·03 mm and sintered at about 1040° C in a hydrogen stove before gold diffusion-soldering is undertaken. This method of diffusion-soldering of copper parts is particularly useful if the envelope concerned is partly of hard glass because the diffusion-soldering at a comparatively low temperature of 400° C can be performed without causing the glass to flow. A.E.I. (Manchester) Ltd. (*BP* 724, 909) give details of the use of silver and copper as intermediaries in place of gold for diffusion-soldering. The metal is electrodeposited onto one or other of the parts to be diffusion-soldered or a foil of about 0·01 mm thickness is used. The surfaces (*e.g.* flanges) to be joined should have two or preferably more circular ridges on them and sufficient pressure should be maintained to cause the metallic members to diffuse into the intermediate metal at the crests of the ridges on heating.

Metal-to-Glass Seals

4.5. Matched and Unmatched Seals

There are two main classes of glass-to-metal seals in which the metal is directly fused to the glass: 'matched' seals and 'unmatched' seals. In matched seals, the stress is minimized by choosing a glass and a metal with coefficients of thermal expansion and contraction which are as nearly as possible the same over the temperature range encountered. In unmatched seals, the thermal expansion coefficient of the metal is different from that of the glass; to minimize the effect of resulting stresses the possible procedures are: (*a*) use metal wires of small diameter or thin metal strips; (*b*) a ductile metal like copper is joined to the glass so that it yields under the stresses produced; (*c*) an intermediate glass is introduced. Of recent years, compressed glass-to-metal seals of the unmatched type have been developed in which thick metal rods are sealed into glass but the stress produced is kept within the breaking stress of the glass chosen.

To choose correctly the appropriate glass and metal to make a matched seal, reference is made to data on thermal expansion coefficients. There are two chief types of glass: soft-glasses and hard-glasses. The former include the soda-lime glasses and the lead glasses. These are readily worked in a gas-air flame though an oxidizing flame must be used for a lead-glass to prevent reduction of the lead oxide. Lead glass has the higher electrical resistivity and is therefore preferred for electric lamp and valve pinches. These soft glasses have a thermal expansion coefficient (α) of between $8·5 \times 10^{-6}$ and 11×10^{-6} per °C over the temperature range from 0° to 100° C. Hard glasses are usually borosilicates and are worked in a gas-oxygen flame. They have thermal expansion coefficients of 3×10^{-6} to 7×10^{-6} per °C.

A metal to be sealed to a glass must have a melting point greater than the working temperature of the glass, should be free from non-metallic inclusions, be available in the form of wire or strip not containing cracks, seams or other mechanical defects, and the metal oxide layer usually formed during the manufacture of the seal should adhere strongly to both glass and metal (Partridge, P5). Breadner and Sims (BS1) recommend that when metal alloys are used for seal-making, each batch of the alloy should be examined to check for consistent physical properties and freedom from mechanical defects.

The data given by Scott (S10) for A.E.I. (Rugby, England) glasses and some sealing metals indicates the importance of referring to the characteristic curves of linear thermal expansion coefficient against temperature (Fig. 4.7) in choosing metal-to-glass combinations. The characteristic is nearly straight for a solid glass up to a transformation region where it exhibits a discontinuity beyond which the curve is again almost straight but with greater slope corresponding to an increased thermal expansion coefficient. For the pure metals the expansion characteristics are almost linear, but for the specially developed glass-sealing alloys, the expansion coefficients increase above a transformation temperature (the Curie point of the ferromagnetic alloy) like the glasses to which they are fused. Comparison of the two sets of curves of

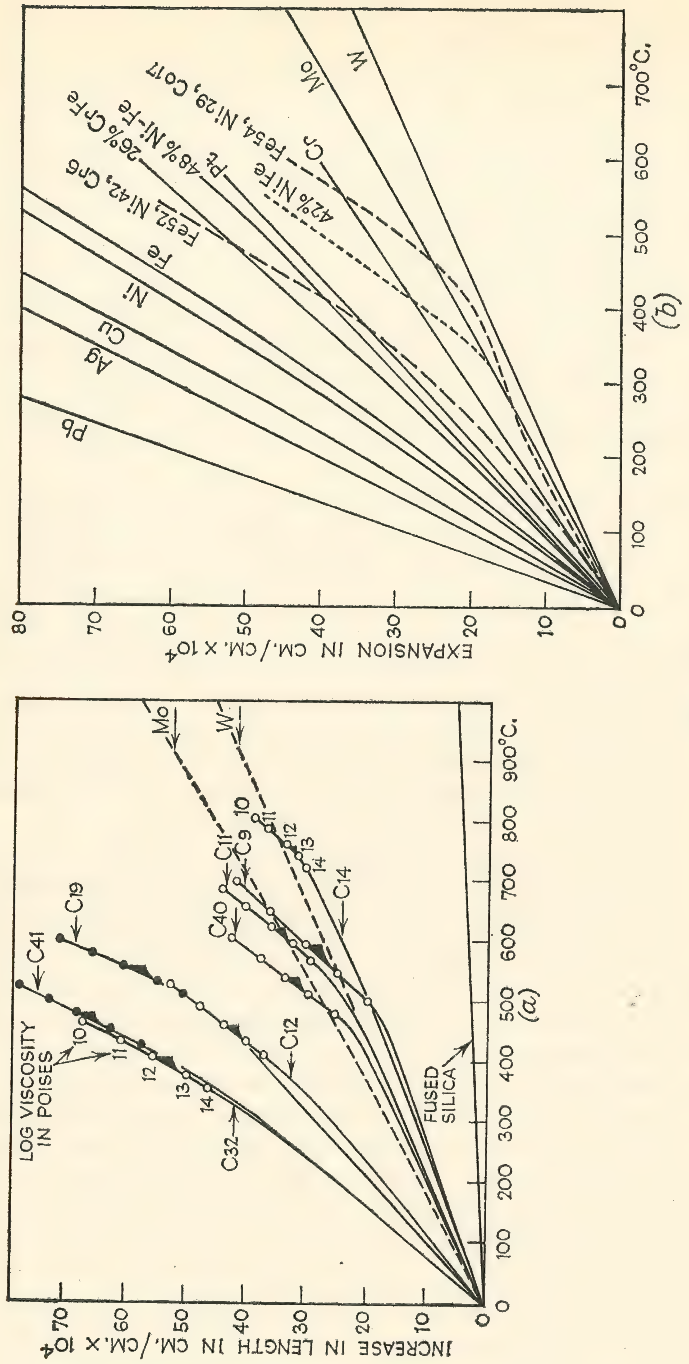


Fig. 4.7

(*a*) Thermal expansion characteristics of some A.E.I. sealing glasses
(*b*) Thermal expansion characteristics of some metals

Fig. 4.7 show the good matches obtainable, for example, between the following combinations: Fe 54, Ni, 29, Co 17 (Kovar) to C 40; Fe 52, Ni 42, Cr 6 to C 12, and tungsten to C 14.

4.6. Metals for Sealing to Soft Glasses

For a detailed account see Partridge (P5). For the physical properties, working and annealing temperatures of the glasses listed the manufacturers' catalogues should be consulted. The state of strain in the annealed seal in the direction at right angles to the axis of a straight through wire or rod in the glass is given from the data provided by Partridge.

Platinum (thermal expansion coefficient $\alpha = 4{\cdot}4 \times 10^{-6}$ per °C). Seals to the soft glasses, in particular, Chance GW1 but preferably GW2, G.E.C. X4 and L1, also Jena 16 III but preferably Jena 2962 III. Bright metallic seal, easily made, the metal being resistant to oxidation, ductile and having very low yield strength. Seal under tensional strain. Wire dia max 1 mm except for preferred glasses where no upper limit. Expense limits application.

Dumet alloy (platinum substitute: Ni 43, Fe 57 sheathed with copper to thickness of about 0·03 mm, usually borated) (longitudinal $\alpha = 7{\cdot}8 \times 10^{-6}$, radial $\alpha = 9 \times 10^{-6}$). Seals in wire diameters up to 1 mm and preferably not greater than 0·5 mm to A.E.I. C12, Chance GW2, Corning G5, G.E.C. L1, Jena 2962 III; seal under tensional strain. Widely used for lead-in wires through glass pinches of radio valves and electric lamps. Platinum sheathed Ni–Fe alloy used where copper would be over-oxidized.

Copper ($\alpha = 17{\cdot}8 \times 10^{-6}$): owing to high ductility can be used for making unmatched seal to many soft and hard glasses if shaped suitably. Melting point at 1083° C somewhat low for sealing to hard glass but nevertheless possible with care. OFHC copper preferred. Feathered edge to copper to provide ready flexibility of metal at joint (Housekeeper, H13). Examples of Housekeeper type and other copper-glass seals are illustrated in Fig. 4.8. These are widely used in specialized electron tube fabrication. Copper becomes brittle unless oxygen-free so it is essential to use neutral, mildly reducing or, best, oxidizing parts of flame (Reimann, R3).

Nickel–iron alloy (Ni 50, Fe 50) ($\alpha = 9 \times 10^{-6}$) to A.E.I. C12, G.E.C. L1, Jena 16 III. Slight tensional strain. Wire dia max 5 mm. As inflection temperature (*cf.* Fig. 4.7) is preferably within the annealing temperature range of the glass, a lower percentage of nickel than 46% is not desirable and seals satisfactorily to soft glasses only. Oxidizes readily in flame but oxide film not strongly adherent. High electrical resistance so heat dissipation for given current capacity is large. Sometimes sheathed with copper to reduce resistance.

Chromium–iron alloy with 26% Cr, ($\alpha = 10{\cdot}2 \times 10^{-6}$) seals to A.E.I. C31, Chance GW1 but preferably GW2, Corning G5, G6 and G8, G.E.C. L14; compressional strain except for G6 glass when tensional. L14 and C31 preferred. Espe (E3) gives detailed account of these alloys. Strongly resistant to oxidation; thin oxide film strongly adherent to metal. Protective oxide film is formed on wire before seal-making either by heating to 950° C in wet hydrogen atmosphere or by pickling in 20% HCl, followed by washing in water (Partridge, P5). Thermal and electrical conductivity low, nevertheless widely used for glass-to-metal seals in, for example, pressed glass, multi-pin bases for electron tubes because resistance to oxygen attack makes this alloy especially suitable for automatic seal-making and machinery where fusion is at high temperature (usually gas-oxygen flame). Examples of chromium–iron alloy to glass seals are illustrated in Fig. 4.9. They are also used in construction of X-ray tubes and large water-cooled valves.

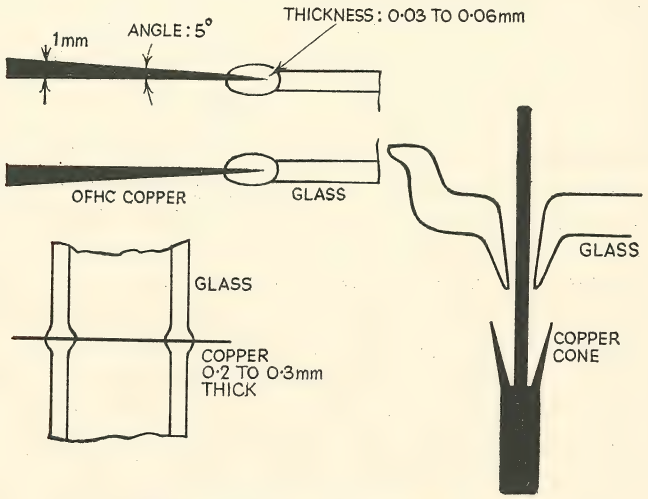


FIG. 4.8 Copper-to-glass seals

Nickel–iron–chromium alloy (Ni 42, Fe 52, Cr 6) ($\alpha = 8\cdot9 \times 10^{-6}$) seals to A.E.I. C12, G.E.C. L1; slight compressional strain. Not so resistant to oxidation as Cr 26, Fe, and oxide film not so strongly adherent. Used in place of Dumet for soft glass seals. Wire oxidized at 1050° C in wet hydrogen atmosphere before seal made.

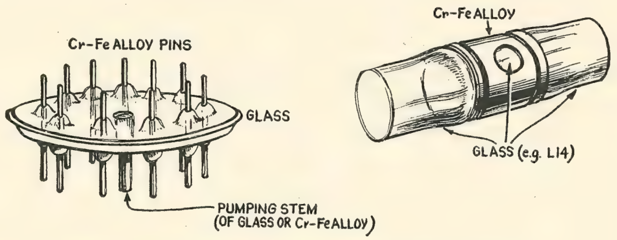


FIG. 4.9 Chromium–iron alloy to glass seals

Fernichrome (Fe 37, Ni 30, Co 25, Cr 8) ($\alpha = 9\cdot95 \times 10^{-6}$) seals to Chance GW2, Corning G5 (slight compression), Corning G8 (compression). Addition of cobalt increases the electrical conductivity of Ni–Fe alloys so heat dissipation in lead-in wire for given current is less.

Many other alloys of iron with nickel and/or chromium and/or cobalt have been used (*see* Partridge, P5; Espe, E3) but those specified above are most usual in practice.

Iron ($\alpha = 13\cdot2 \times 10^{-6}$): the special glasses G.E.C. R16 and A.E.I. C76 have been developed for sealing directly to pure iron. Rusting is considerable difficulty. For copper-plated iron, A.E.I. C41 can be used.

4.7. Metals for Sealing to Hard Glasses

Tungsten ($\alpha = 4\cdot4 \times 10^{-6}$) seals to several borosilicate glasses but preferred glasses giving least strain, especially for large diameter wires, are A.E.I. C14, Chance GS1 ('Intasil'), Corning 371 BN ('uranium glass'), G.E.C. W1, and Jena 1646 III (tungsten-sealing glass). For wires of diameter not greater than 2 mm: A.E.I. C9 (slight compression), Chance GH1 ('Hysil': with care: severe compression), Corning 726MX (severe compression), Corning G702P ('Nonex'; compression), G.E.C. WQ 31 (severe compression), Jena 8212 III (4 mm dia wire max), Jena 3891 III (max 3 mm), Jena 8330 III and 2955 III (max 1 mm; compression), Pyrex (severe compression). Tungsten is hard, brittle and difficult to work; should be ground rather than cut mechanically. Oxidizes easily but oxide film only reasonably adherent.

Molybdenum ($\alpha = 5\cdot5 \times 10^{-6}$): preferred glasses are A.E.I. C14, Corning 704, Corning G71 (slight tension), Chance GS4 (Mo–GS4–GS1–GH1 is recommended combination for Mo to Hysil), Jena 1639 III; further glasses, less recommended, are A.E.I. C11 (compression), Corning 705 AJ (severe compression), G.E.C. HH (compression), G.E.C. H26 (severe compression), Jena 8401 III and 1447 III (wire dia max 3 mm). More ductile than tungsten but not readily worked. Easily oxidized and oxide film non-adherent, therefore access of air restricted in seal-making. Partridge recommends fusing closely-fitting glass tube to molybdenum rod and sealing progressively from one end to the other so as to expel air from annular space between rod and glass.

Adam (A4) describes the manufacture of matched seals between Kodial glass (*Plowden and Thompson Ltd.*) and molybdenum rods of up to 100 mm dia and of annular seals of molybdenum (*e.g.* in the form of a cap) to this glass of up to 75 mm dia. The necessary fusion is arranged by a suitably disposed graphite block around the seal of which the temperature is raised by r.f. induction heating.

The alloys most frequently used to replace the difficult tungsten and molybdenum for hard-glass sealing are Fernico and Kovar, which are similar but not identical.

Fernico I (Fe 54, Ni 28, Co 18; $\alpha = 4\cdot5 \times 10^{-6}$) and **Kovar** (Fe 54, Ni 29, Co 17; $\alpha = 4\cdot7 \times 10^{-6}$) both seal readily to A.E.I. C40, Chance GS3 (to seal to Hysil, recommended combination is Fernico I to GS3–GS4–GS1–GH1), Corning 705 AJ (compression), Corning 705 AO or G71 (slight tension). Widely used; *see* Fig. 4.10 for examples of practice. Lower yield strength and greater ductility than tungsten or molybdenum. Also, as Fernico type alloys have thermal expansion characteristics with a transition temperature in about the same region as the sealing glasses, these seals are much less sensitive to the cooling than are tungsten seals.

For a full discussion of the effects of adding cobalt to iron–nickel alloys, *see* Partridge (P5).

Fernico II (Fe 54, Ni, 31, Co 15; $\alpha = 5 \times 10^{-6}$) gives strain-free matched seal to Corning 705AO.

Other Kovar type alloys suitable for hard-glass sealing to B.T.H. C40 and G.E.C. FCN are Nicosel, Telcoseal No. 1, Darwin's F alloy and Nilo K. There is no difficulty in soldering, brazing or welding these alloys but silver-soldering renders them porous.

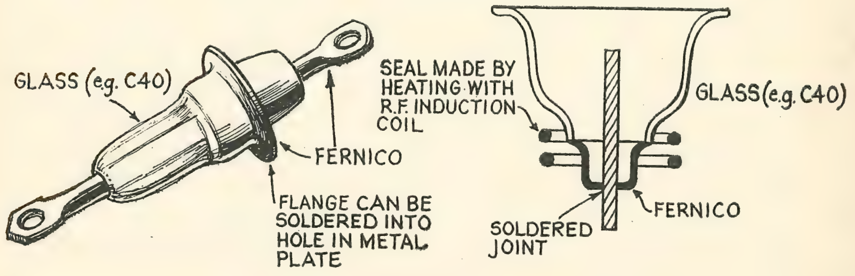

GLASS (e.g. C40)
FERNICO
FLANGE CAN BE SOLDERED INTO HOLE IN METAL PLATE
SEAL MADE BY HEATING WITH R.F. INDUCTION COIL
GLASS (e.g. C40)
SOLDERED JOINT
FERNICO

FIG. 4.10 Fernico-to-glass seals

Rawson and Denton (RD1) discuss the glass-sealing properties of titanium and zirconium which have become commercially available of recent years in the form of wire and tubing. The linear thermal expansion coefficients are between 5×10^{-6} and 10^{-5} per °C, with considerable variations depending on the source of the material and the heat treatment adopted. The wires need no treatment beyond rubbing with fine emery paper and the recommended glasses are A.E.I. C40 for zirconium and A.E.I. C77 and C78 for titanium. The present high cost of these metals limits the possible application. Moreover, as pointed out by Partridge (P5) in connection with the possibilities of tantalum to glass seals, these metals absorb gases very readily.

4.8. Metal-to-Silica Seals

Tungsten wires can be sealed into silica ($\alpha = 0{\cdot}5 \times 10^{-6}$) by the use of intermediate borosilicate glasses of high silica content and containing little or no alkali. Partridge (P5) lists the compositions of twelve glasses with expansion coefficients between 1×10^{-6} and $3{\cdot}6 \times 10^{-6}$. The silica is first joined to the lowest expansion glass (*e.g.* G.E.C. WQ31), then via two further glasses of intermediate expansions to the tungsten. Partridge also illustrates a seal comprising a tungsten rod passing through the dome-shaped end of a silica tube where only one intermediate glass is used between the silica and the tungsten. Specially constructed electric or gas furnaces are needed to provide the temperatures of the order of 2000° C needed to fuse these low expansion glasses. Molybdenum ribbon of thickness not greater than 0·02 mm can also be directly fused to silica to give an unmatched seal. A type of silica-tungsten or molybdenum seal which has been used in silica envelope transmitting valves was developed by Sands and is described by Partridge. Molten lead is used to seal the gap between the wire and the surrounding close-fitting silica tube. To make this seal, the arrangement shown in Fig. 4.11 is first evacuated, the constricted part of the silica tube collapsed on to the molybdenum wire by heating and, whilst the silica is hot, the lead is melted to flow down into the space around and above the wire. On breaking the top of the glass tube, air is admitted which forces the lead into contact with the wire and the silica to provide a vacuum-tight seal. A tinned, flexible copper conductor is usually inserted into the lead as it solidifies.

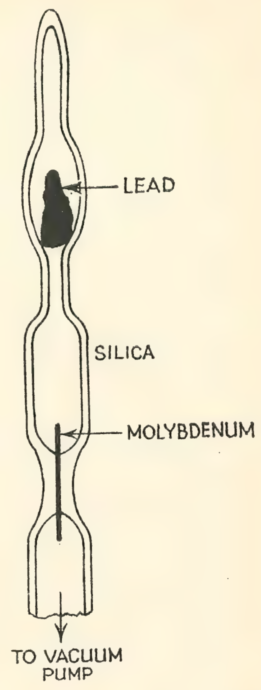


FIG. 4.11 Seal between molybdenum and silica by use of lead

4.9. Compressed Glass-to-Metal Seals

Adam (A5) gives references to previous work and discusses from the theoretical and practical points of view the fabrication of window-seals consisting of a circular slab of glass of diameter as much as 10 in. within a metallic ring and also such seals containing one or more inserted metal rods or tubes for use in large mercury rectifiers. A window-seal is often made from a standard soda or lead glass with an external ring of matched nickel–iron or chromium–iron alloy (*see* § 4.7). It is, however, difficult to weld such alloys into a mild steel envelope wall of, for example, a steel tank mercury rectifier, so the use of unmatched seals between glass and mild steel is attractive. In such an unmatched seal (Fig. 4.12(*a*)) the thermal expansion of the surrounding metal ring is greater than that of the glass and the glass window is consequently under compression in all directions and the outer metal is under tension at its inner surface. Calculation shows, however, that the compression in a glass window within a mild steel ring is considerably below the compression strength of the glass for any practicable combination of glass and metal. Nevertheless, there is a possibility of over-stressing the outer metal

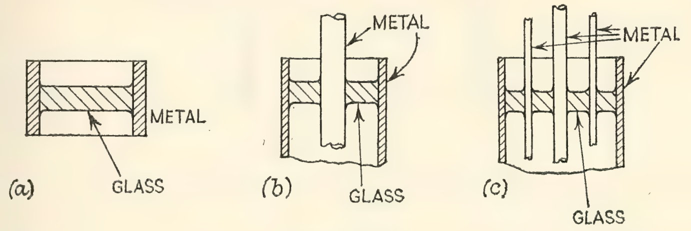


FIG. 4.12

(*a*) Window seal with glass under compression
(*b*) Window seal with one central rod
(*c*) Window seal with three rods

which will lead to such non-uniform stresses in the glass that it will crack unless the glass piece is shaped to avoid disruptive shearing stresses on the free surface. A suitable design of window-seal where these stresses are below the safety limit is shown in Fig. 4.13.

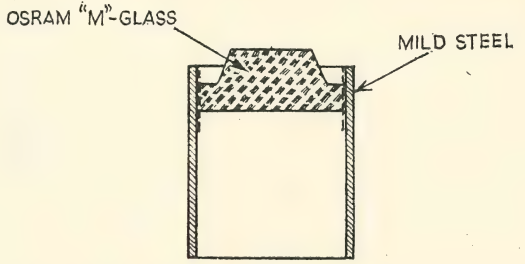


FIG. 4.13 Specially shaped unmatched window seal between lead glass and mild steel

Of greater technical importance than the window-seal is one with a central metal rod for current carrying (Fig. 4.12(*b*)). This central rod can be of an alloy like nickel–iron or chromium–iron which is matched to the glass although the outer ring is of mild steel. The compression in the glass will, however, be increased compared with the case of the simple, two-component window seal because the modulus of elasticity of the metal of the rod is usually much higher than that of the glass. Nevertheless, such three component seals can be made in a wide range of overall dimensions. Adam recommends an outer metal ring of mild steel of low carbon content, a disc with central hole of lead glass containing about 31% PbO and the central rod or tube of a chromium–iron alloy with 19% chromium. The outer radius of the glass should be twice that of the metal rod while the wall thickness of the metal ring should not exceed 2 mm. The seal shown in Fig. 4.14 is designed for very large current capacities: the outer ring is mild steel, a 19% chromium–iron alloy tube is sealed into the central hole in the lead glass disc and a central rod through the bore of the alloy tube is hard-soldered to it at the outer end. For seals with more than one metal rod (Fig. 4.12(*c*)) Adam concludes that if the distance between each rod and its neighbours and the outer wall is equal to or greater than its diameter, then no rod will be affected by any other.

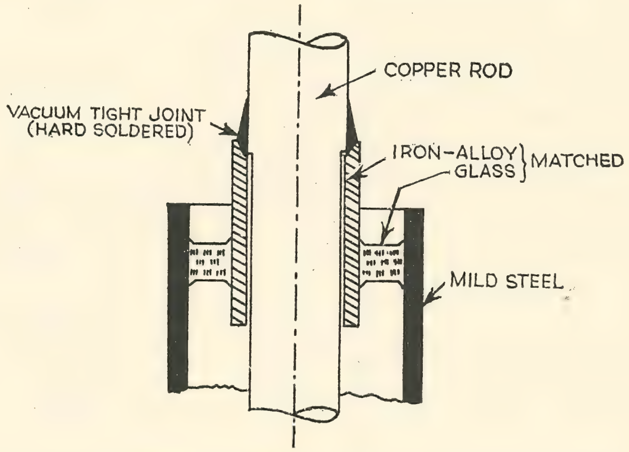


FIG. 4.14 A compressed glass-to-metal seal for heavy currents

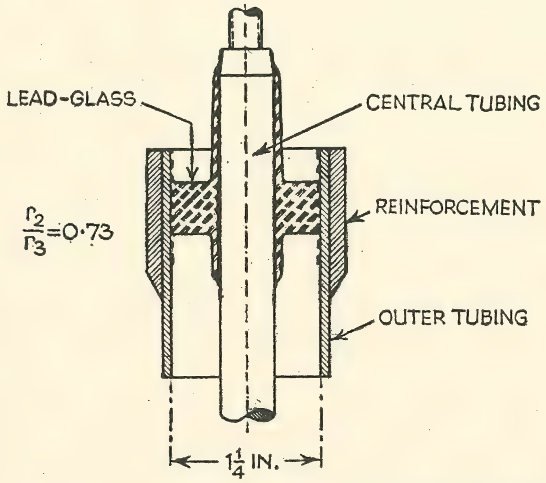


FIG. 4.15 Compressed lead glass-to-metal seal with unmatched central rod and outer ring of mild steel

It is also possible to use an unmatched inner rod or tube, *i.e.* where the central rod and the outer ring are both of mild steel. Calculation shows that the tension at the inner-glass–metal boundary depends markedly on the thickness of the outer metal ring. Indeed, a formula can be derived for the *minimum* thickness of the outer metal ring required *to reduce the tension in the glass to zero*. The glass is then in a safe condition provided that it is under compression in all directions. For mild steel and glass $\left(1 - \frac{r_2}{r_3}\right)$ is about 0·23 where r_2 and r_3 are the inner and outer radii respectively of the outside metal ring. Hence, for an inner diameter of 55 mm, the minimum wall thickness of the metal ring is 7·5 mm. This result is independent of the diameter of the central metal rod. Fig. 4.15 shows a design due to Adam in which, to achieve the required wall thickness, an annular reinforcement is shrunk on to the outer tubing and the central metallic member is a tube, whilst Fig. 4.16 shows a much larger seal in the form of a cathode pool of a mild steel tank mercury rectifier.

Three component glass-to-metal seals with an unmatched mild steel outer ring and a matched central alloy rod have been widely used in metal thyratrons and steel-tank rectifiers but the unmatched three-component compression seal, though of considerable promise, has not yet been used in routine production (Adam, A5).

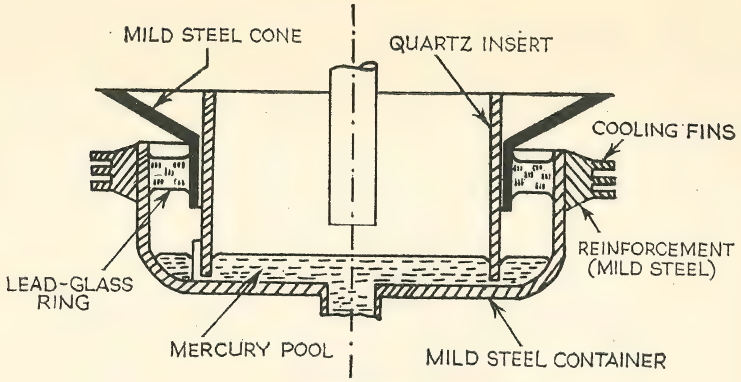


FIG. 4.16 A mercury pool cathode (*Adam*)

4.10. Soldering to Glass

Two procedures are of value: the use of 'glass-solders' to join glass to glass or glass to mica, and the use of metallic solders to join a metal to a suitably metal-coated glass.

The use of glass-solders enables vacuum-tight seals to be made between glass parts and is of particular application when the direct fusion of the glass parts by glass-blowing is difficult. Examples are the joining of a flat polished glass window to a spherical bulb and the sealing of a pressed glass base containing sealed-in metal leads to an electron tube envelope. These glass-solders have low deformation temperatures compared with the usual soda–lime and lead glasses. They have a small silica content and consist largely of lead oxide, boron oxide and zinc oxide. Examples are given in Table 4.10 (*see also* Steyskal, S9).

TABLE 4.10
Glass-solders

Firm	Glass	Soldering temperature, °C	Linear thermal expansion coefficient
General Electric Co., Ltd. (England)	GSS 38	475	$9{\cdot}5 \times 10^{-6}$
	GSS 34	525	$9{\cdot}8 \times 10^{-6}$
	GSS 1	500	$8{\cdot}0 \times 10^{-6}$
Associated Electrical Industries Ltd. (Rugby, England)	PZS 2	550	$9{\cdot}0 \times 10^{-6}$
Telefunken (Germany)	T 209	410	$9{\cdot}0 \times 10^{-6}$
Fischer	F 3	540	$9{\cdot}0 \times 10^{-6}$
	140 3	620	$5{\cdot}0 \times 10^{-6}$

It is to be noted that the expansion coefficients of these glass-solders are best suited to the soft glasses. They are supplied in the form of a water-bound paste of the glass powder. Experience is necessary to ensure a satisfactory seal.

The best practice is to use a thermostatically controlled electric furnace for heating and to undertake tests to ensure the best curing and annealing times to prevent fracture on cooling or 'crazing' of the glass-solder.

To join metal to glass it is possible first to coat the glass with a layer of metal and then solder to the metal component. The metal layer on the glass is preferably of silver, silver–copper, platinum or gold. Silver films can be deposited on glass by evaporation *in vacuo* (§ 10.4) or by cathodic sputtering (§ 10.10), but they are not really sufficiently adherent to withstand a subsequent soldering process. Platinum can be evaporated with difficulty but is preferably sputtered. A sputtered film of platinum on glass which is then sintered is strongly adherent, but this process is elaborate compared with the simple and most usual procedure of using a painted-on suspension of the metal in an oil-base. In general, therefore, the best procedure for joining, say, a glass to a metal tube by a soldering technique is to roughen with emery cloth the end of the glass tube where the soldered joint is to be made, clean it thoroughly in chromic acid, wash and dry, then paint on the appropriate part a suspension of finely divided silver, gold or platinum in lavender oil, with silver preferred for ready soldering, and fire this deposit at 550° for soft glass and 700° C for hard glass in an electric furnace (with air admitted to ensure oxidation of the evaporated organic liquid) to leave a firmly adherent metallic film. Partridge (P5) points out that silver films produced in this way should appear yellow on viewing through the glass, showing that silver ions have migrated satisfactorily into the glass.

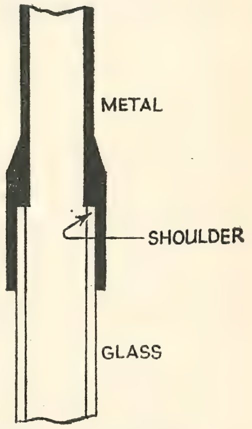


FIG. 4.17 Soldered glass-to-metal tubes

A suitable glass-to-metal tube soldered joint is best arranged as in Fig. 4.17 (Partridge, P5) where a shoulder is fashioned within the metal tube against which the glass tube is butted. The clean metal film on the glass should not be directly tinned as this may remove it. Rather, the inside wall of the metal tube (radius 0·5 mm greater than that of the glass tube) should be first tinned, slid over the glass, and the union heated to just above its flow point. McKelvy and Taylor (MT2) recommend tin solder with zinc chloride as flux, but tin–lead solders containing 2% silver are better for soldering to silver. Copper-plating the silver film before soldering is advantageous. Ridyard (R9) prefers the rather more difficult process of first platinizing the tube, dipping it momentarily in molten lead, coating with 'Fluxite' and then soldering to the tinned metal tube. More recently Belser (B16) has stressed the advantages of using indium and its alloys as solders which possess remarkable adhesive properties to a wide range of metals, glass, quartz and other siliceous materials, ceramics and metal oxides, even without the use of flux. The melting point is 155° C. To join an electric contact lead to a metal film on glass, the recommendation is to use a pure tin on gold film on the glass and then make the indium soldered joint using a standard pencil-type soldering iron. The temperature is critical for correct wetting by the molten indium; no flux is necessary provided the surfaces are clean. Silver and lead alloys of indium are preferred as they possess greater hardness and strength than the pure metal; a 5% silver–indium alloy is best for soldering to thin silver films to prevent solution of the film in the solder.

Johnson, Matthey and Co., Ltd. supply the following materials for coating glass or ceramics:

Silver pastes X.351 and X.353 used in sequence enable a thick silver film to be deposited. X.351 contains a bonding agent that fuses into the cleaned glass or ceramic surface during firing. This layer is then covered with a coat of X.353 which consists of a fine suspension of finely divided pure silver (paste is pink to avoid confusion). Both pastes are thinned so that they can be applied with a brush: thinner 9870 is used for X.351 and thinner 7902 for X.353. The X.351 coat should be allowed to dry before applying X.353, firing is then at 550–700° C (for glass, at 20° C below its softening point). Parts should be put in a ventilated furnace at a temperature below 100° C and heated slowly to firing temperature, at which they should be maintained for 20 min. Tinning with soft silver solder (Table 4.2) is recommended and subsequently ordinary tin–lead, with a melting range of 183–250° C, is especially recommended. A resin-base flux should be used.

Six flake silver type metallizing preparations are also available. Of these, four are listed in Table 4.11.

TABLE 4.11
Flake silver metallizing preparations

Ref. No.	Suitable for	Method of application	Remarks
FSP.3	Mica, glass, glazed ceramics	Brushing	Use white spirit as thinner; alternative to X.351 plus X.353
FSP.4	Unglazed ceramics	Brushing	Use white spirit as thinner; alternative to X.351 plus X.353
CSP.5[1]	Mica, glass, glazed ceramics	Spraying	Turpentine used as thinner
CSP.6[1]	Unglazed ceramics	Spraying	Turpentine used as thinner

[1] Contains a mixture of flake and colloidal silver.

Heat for 5 to 10 min over range 200–450° C and then more rapidly (if required) to maximum firing temperature which is maintained for 10–20 min. Firing temperatures recommended are: soda–lime glass, 560–570° C; hard glass, 600° C; mica, 540° C; glazed ceramics, 600–670° C; unglazed ceramics, 720° C.

TABLE 4.12
Platinum, gold and palladium metallizing preparations

Ref. no.	Suitable for	Method of application	Firing range °C	Remarks
Platinum paste T 177	Heat-resisting glasses	Brushing	600–650	Strongly adherent
Platinum paste N 758	Unglazed refractory ceramics	Brushing	700–1500	For parts to be used at high temperature
Liquid matt platinum 121235G	Glass	Brushing or spraying	700–900	
Liquid platinum F 104	Glass	Brushing, dipping or spraying	560–650	Excellent for glass
Liquid platinum 7%, for ceramics	Glazed ceramics	Brushing, dipping or spraying	650–800	
Liquid bright platinum Ga	Glass	Brushing, dipping or spraying	520–650	Gold platinum alloy film
Liquid bright platinum G	Glazed ceramics	Brushing, dipping or spraying	650–800	Gold platinum alloy film
Liquid bright gold 12%, C	Glass	Brushing, dipping or spraying	520–650	
Liquid bright gold 12%, Y	Glazed ceramics	Brushing, dipping or spraying	650–850	
Palladium paste A 286	Unglazed refractory ceramics	Brushing or spraying	700–1500	High temperature use
Liquid palladium 4½%, for glass	Glass	Brushing, dipping or spraying	560–650	
Liquid palladium 3349	Glazed ceramics	Brushing, dipping or spraying	650–800	

A range of platinum, gold and palladium preparations is available (Table 4.12). They are solutions or suspensions of precious metal compounds combined with adhesion promoting agents in organic liquids. Application to glass or ceramic is by brushing, spraying, dipping, stamping or screen printing. Thinners are not normally necessary but thinner R.60 can be used with the platinum and palladium pastes and Essence 25 or 58 for the others. As palladium begins to oxidize at 400° C, an inert or reducing atmosphere should be used during the final stages of firing.

Ceramic-to-Metal or Glass Seals

4.11. Ceramic-to-Metal Joints*

Techniques for making vacuum-tight seals between ceramics and metals have been developed in recent years, particularly for the fabrication of ceramic envelope thermionic valves of special types, *e.g.* for ultra-high frequency working. The advantages of ceramics over glass in this respect are: (*a*) degassing bakes at temperatures up to 700° C are possible, and the getter is then not necessary in some cases; (*b*) the operational temperature of the valve can be increased; (*c*) precision grinding of ceramic permits closer tolerances in the envelope manufacture and more accurate electrode assembly; (*d*) mechanical robustness; (*e*) small dielectric losses for u.h.f. operation. The disadvantages are: (*i*) seals made must be under compression, so the assembly to be soldered must be arranged so that it is always under pressure; (*ii*) the envelope is opaque; (*iii*) specialized procedures are necessary for seal-making.

Originating in Germany, the techniques of ceramic-to-metal seal-making have been developed there, in America and later in Britain. The two most frequently used methods in the fabrication of specialized types of thermionic valves are (1) **the molybdenum–manganese process** and (2) **the zirconium hydride process.**

The American development of method (1) from the procedure initially due to the Telefunken laboratories in Germany, is first to clean the ceramic chemically and then paint or spray on the appropriate portion to a thickness of 0·001 to 0·002 in. a mixture of finely divided molybdenum plus 10% manganese powder (particle diameter: 2 to 5 micron) in the form of a paste in water or a nitrocellulose binder, dry in air and then sinter in wet hydrogen at a temperature within 50° C of the softening point of the ceramic (*i.e.* usually at about 1400° C). A firmly bonded conductive coating is produced which is then electroplated with copper or nickel to improve the solder-wetting properties, and then re-sintered as before. The joint to the metal part is then made by silver-soldering in a hydrogen atmosphere. Other metal mixtures have been used, *e.g.* 10% Mn with tungsten, iron or nickel; 20% Mn with Mo, and also pure metal powders such as Mo, W and Rh.

In the zirconium hydride (ZrH_4) process, the cleaned ceramic is coated with a thin layer of a paste made from powdered zirconium hydride in water or nitrocellulose binder, allowed to dry, and a ring or other appropriate shape of pure silver solder (or silver–copper eutectic) is placed in contact with this layer. The metal part is then put in position and the assembly inserted into a vacuum stove (pressure $< 10^{-4}$ torr) and induction-heated to 1050° C by use of a suitably disposed outside coil carrying current. The ZrH_4 disintegrates before the solder melts, the hydrogen is pumped away and the remaining zirconium forms a strongly bonded surface film on the ceramic and alloys with the silver soldered to the metal member. This process is often known as the Bondley technique (B17), though Bondley used titanium hydride, which is not preferred. Brand, Jacobs and Lo Cascio used this Bondley technique with ZrH_4 for circular seals between the ceramic Alsimag 243 (American Lava Company) and nickel–iron alloy and also for a ceramic Zi4 (Coots Porcelain Company, U.S.A.) which has a zirconium silicate base, to Kovar or, to a greater extent, molybdenum. The ceramic cylinder was coated with ZrH_4 and a ring of silver wire was placed around the cylinder near the end to be sealed. This assembly was put on a metal disc and lowered into a carbon crucible suspended in a glass tube which could be evacuated. The carbon was then heated by h.f. currents from an external induction heater coil. A glass 'umbrella' was used to protect the inner wall of the glass tube from silver deposited during the sealing process. A quicker process is to place the assembly in an atmosphere of dry hydrogen, nitrogen or neon in a silica tube and heat by an oxygen-gas flame, but the seals produced are of inferior quality. For making ceramic diode valve envelopes, Jacobs and Lo Cascio recommend Alsimag 243 to a nickel–iron alloy and report that the chief difficulties with the diodes produced were electrical leakage due to condensed Zr–Ag vapour.

TABLE 4.13
Ceramic-to-metal combinations

Ceramic		Metal
Type	Name	
Forsterite	Alsimag 243	50% NiFe 46% NiFe 16% CrFe
Steatite	Alsimag 196 Telefunken laboratories	Kovar 42% NiFe 46% NiFe
Zircon	Z17A Z14	Molybdenum Molybdenum Kovar
Alumina	Alumina Al 200 Alsimag 491 Alumina 2548	Copper; Nickel Kovar 44% NiFe 44% NiFe

The rates of heating and cooling during the soldering process must be carefully controlled.

It is not easy to select ceramics with thermal expansion coefficients which match metals over the wide temperature range involved and which also have desirable electrical and thermal properties. Suitable ceramic-to-metal combinations for matched seals are listed in Table 4.13 (Jenkins, J4). For unmatched seals the thickness of the metal at the joint should not exceed 0·2 mm (*cf.* the Housekeeper seal, § 4.6). A ductile metal ring can be used as an intermediate between the ceramic and metal parts for large diameter assemblies.

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* Jenkins, J4; Steyskal, S9; Partridge, P5; Brand, Jacobs and Lo Cascio, BJL1; MIT. 1.

Of these ceramics, Alsimag 243 and alumina have been most widely used because of their low dielectric loss and low thermal expansion.

Doolittle (D6) prefers the molybdenum–manganese process for small, low voltage, assemblies and the hydride process for large assemblies. Jenkins (J4) illustrates u.h.f. valves, klystrons and an X-ray tube in which ceramic-to-metal seals are used. U.h.f. thermionic valves with direct copper-to-ceramic seals have also been made commercially.

4.12. Ceramic-to-Glass Seals *

Ceramics which have suitable thermal expansion characteristics to enable them to be sealed to hard glasses are chiefly based on china clay (porcelains), sillimanite and zircon. Moulded shapes of china-ball clay refractories fired to at least 1400° C may be fused to Pyrex or Hysil glass to give a seal in longitudinal compression or to G.E.C. W1 glass to give a seal in tension. These ceramics suffer shrinkage at the necessary high firing temperatures and have poor resistance to thermal shock. This shrinkage and cracking risk may be reduced by the addition of finely-ground calcined china clay. The addition of magnesia, zirconia or feldspar raises the thermal expansion of the clay refractory to provide a better matched seal to glasses like G.E.C. W1. Sillimanite-clay refractories can also be sealed to these borosilicate glasses. Their resistance to thermal shock is high, they undergo little shrinkage on firing to 1400° C or more, but need to be glazed (*e.g.* with W1 glass) to render them non-porous. Zirconium silicates can also be used.

Mullite tubes (Thermal S25 Mullite; Thermal Syndicate Ltd., and H5 Mullite; Morgan Crucible Co., Ltd.) seals satisfactorily to G.E.C. W1 glass (Kent, K8). Very robust seals capable of withstanding temperatures up to 550° C can be made in diameters up to 2 in. using a bench blow-pipe, whilst larger seals up to 3 in. dia are best made in a glass-blowing lathe. For diameters exceeding 1 in. the Mullite tube should have a wall thickness of at least $\frac{1}{4}$ in.; heating and cooling must be gradual to avoid cracking due to thermal shock. The Mullite is best cut with a nichrome wire charged with carborundum-glycerine paste. W1 glass can also be sealed to Morgan ΔCC (bonded silicon carbide) and ΔH (aluminous porcelain).

Ceramics which are suitable for sealing to the high expansion soft glasses like G.E.C. L1 are combinations such as steatite–magnesia, steatite–zirconia and magnesia–beryllia. Partridge tabulates the compositions of these combinations necessary to give the correct thermal expansion coefficients. The beryllia-bearing ceramics offer the best resistance to thermal shock, though these seals will be more subject to this difficulty than the low expansion ones.

Recently, stabilized (*i.e.* recrystallized) sintered glass cements, known as 'Pyroceram' have been produced by the Corning Glass Works. They are vacuum-tight and some of them are serviceable up to 700° C. They are applicable to glass, ceramic and metal joints. Also, a high melting point glass (No. 1723) for sealing to molybdenum and with extremely low helium permeation is offered.

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* Partridge, P5.

Bonding of Polyethylene to Materials

4.13. Polyethylene (Polythene, Alkathene, Hostalen)

Plastics may sometimes be used in place of glass or metal in the design of vacuum plant. The vacuum applications of polythene are described by Duncan and Warren (DW1). Polythene tubing of internal diameter not greater than $\frac{1}{2}$ in. and wall thickness $\frac{1}{8}$ in. withstands evacuation without collapsing, though for diameters of up to 3 in. a wall thickness of $\frac{3}{8}$ in. is usually necessary.

If the inner wall surfaces are clean it is possible to obtain with sufficient pumping speed pressures of 10^{-6} torr within polythene vessels after pumping for about 30 min. Adsorbed gases will, however, be evolved for several days and, moreover, this plastic is slightly permeable to gases and water vapour. Even so, a pressure of 10^{-4} torr can be maintained overnight in a clean polythene vessel sealed from the pumps. As the melting point of polythene is 110° C, baking is not readily possible, so that the use of a discharge excited by a Tesla coil is recommended to assist the release of occluded gases.

A joint in polythene tubing or of tubing or thin sheet to glass or metal may be easily formed by heating with a jet of hot nitrogen. A stream of nitrogen passed through a tube electrically heated to about 200° C forms a simple and adequate means of making the joints, which can be fashioned without special manipulative skill. This technique is especially useful in constructing vacuum plant where the tubing on the backing pressure side is of polythene instead of rubber, glass or metal. Joints between tubes of metal, glass or ceramic and polythene may also be made by heating the end of the refractory tube to above the softening point of polythene and inserting into the polythene tube. The junction is then warmed gently (*e.g.* with the nitrogen torch) and as the polythene begins to flow it is pressed by a flat, cold metal tool to ensure a vacuum-tight seal of good bonding properties.

Polythene can be machined, but the accuracy achievable is limited by a tendency to flow, although this is not serious in apparatus not subject to mechanical stress. If such stress is inevitable, a harder plastic like polytetrafluoroethylene (Teflon) is preferable. Metal and glass components can also be coated with chemically resistant polythene which is available in powder form; the component is heated to about 200° C, simply plunged into the powder and then subsequently heated to about 120° C. To bend polythene tubing, the nitrogen torch may be employed, but a useful technique is first to insert a strong coil metal spring support and immerse in hot water for about 15 min; the tubing can then be bent to the desired shape which it will retain on cooling. To fabricate vessels up to 6 in. in diameter, polythene tubing of $\frac{1}{2}$ in. wall thickness can have end-plates fused on by means of the nitrogen torch. Isolation valves, gas-metering valves, taps (§ 5.7) and even manometers can all be fashioned from polythene. Cold traps can also be made of polythene, but they will shatter at liquid air temperatures unless they are stress-relieved and designed to avoid steep temperature gradients. To make a polythene liquid air trap, therefore, it is necessary to machine it from a solid block of polythene and fuse on the necessary polythene tubes by using the nitrogen torch. The poor thermal conductivity of this plastic means, however, that such a liquid-air trap will be inefficient.

Small leaks in polythene tubing can be sealed up *in situ* without admitting air to the vacuum plant. Fresh polythene is melted and pressed with a cold flat tool on to the area of the leak.

Polythene grease is also available. This and the tubing, sheet, etc., are available from I.C.I. Plastics Division. More recently this firm has offered Polypropylene, which melts at 163° C and is more rigid than polythene.

Permanent and Semi-Permanent Waxed and Cemented Seals

4.14. Waxes and Cements

Vacuum-tight joints between refractory materials like glasses, metal and ceramics of a more or less permanent character can be made by raising the temperature of the components and applying a wax or cement. The commercially available vacuum waxes of low vapour pressure like Picein and the W-waxes (Table 4.14) are suitable for semi-permanent joints where the temperature increase allowable is limited, but for permanent seals where higher temperatures can be used during fabrication and where some degree of degassing by baking is possible, the epoxy resins, in particular, Araldite, are strongly recommended. Cold-setting Araldite is also available.

TABLE 4.14
Waxes, cements and adhesives

Material	Softening temp. °C	Vapour pressure torr	Remarks
Apiezon 'Q' compound	20 to 30	Order of 10^{-4} at 20° C	Plasticine-like mixture of graphite and paraffin oil distillation residues. Can be pressed with fingers round joint to make temporary seal
Apiezon W wax Apiezon W40 wax Apiezon W100 wax	60 30 50	10^{-6} at 20° C 10^{-3} at 180° C	W40 used where temperature of parts must be kept low. Black waxes available in sticks. Soluble in xylene. W40 and W100 less brittle than W
Araldite	120	2×10^{-7} at 20° C	Curing process necessary (*see below*). Available in sticks or powder form. Cold-setting Araldite also available (*see below*)
Edwards W.E. wax 3 Edwards W.E. wax 6	80 90	10^{-6} at 20° C 10^{-6} at 20° C	Shellac-based brown wax soluble in alcohol (unlike Apiezon W and Picein). Fairly insoluble in benzene, toluene and other aromatic hydrocarbons. Available in sticks. Product of Edwards High Vacuum Ltd. W.E. 6 has been much used for sealing strain-gauge wires

TABLE 4.14 *continued*

Material	Softening temp. °C	Vapour pressure torr	Remarks
Khotinsky cement	50	10^{-3} at 20° C	Mixture of shellac and pitch obtained from Caroline tar. Comparatively insoluble in common organic liquids and acid-resistant. Available in sticks
Myvawax S	70	10^{-6} at 20° C	Soft hydrocarbon wax which is soluble in petroleum ether, CCl_4 and benzene. Unaffected by acetone, alcohol and pump oils
Picein	50	10^{-6} at 20° C	Flows free at 80° C. Yields sufficiently at 15° C to prevent cracking in use. Soluble in benzol and turpentine. Inert to alcohol and inorganic acids. Available in sticks; used like the Apiezon W wax
Silver chloride	Applied at 450° C	Negligible at 20° C	Useful sealing cement for withstanding high temperatures; used for sealing small flat windows on glass tubes, seals into discharge tubes. Soluble in sodium thiosulphate
Zinc oxychloride			Dental cement: 60% zinc chloride with zinc oxide powder mixed in form of thick paste

The Apiezon W waxes and Picein are available from Edwards High Vacuum Ltd. in Britain and from J. G. Biddle Company, Philadelphia, in the U.S.A. Picein is also marketed by Leybold in Germany, who supply in addition a white sealing-wax and a vacuum cement called Desmodur. Khotinsky cement is marketed by Edwards High Vacuum Ltd. in Britain and a modified form with lower vapour pressure and higher mechanical strength is obtainable from the Central Scientific Company in the U.S.A. In general, these waxes have similar uses, *i.e.* the ready manufacture of semi-permanent seals between cones, flanges or flat surfaces of metals, glasses, quartz and ceramics. The parts to be joined as well as the wax should be heated to just above the softening temperature of the wax if an adhesive vacuum-tight seal is to be obtained. The seal can be dismantled easily on the application of heat, but this proces is necessarily messy. These waxes can so be used for making temporary seals over pin-holes, porous parts or leaky joints in vacuum plant. For small-scale laboratory plant their use is often convenient, especially on the 'backing' side, but plant for continuous long-term use is best designed to avoid the permanent application of these waxes.

Araldite (Ciba (A.R.L.) Ltd.) is a most valuable bonding material which is much used in the aircraft industry, and in the electrical industry as a casting resin. As a cement for joints between parts of vacuum apparatus it has been used in many applications. The thermo-setting Araldite Type 1 is the most suitable form; it is available as sticks or powder. The surfaces to be joined may be of metal, glass, ceramic, quartz or mica and must be cleaned thoroughly. Excellent adhesion is obtained if the Araldite powder is first sprinkled over the surfaces and then heated—without pressure being necessary—at 240° C for 10 min. Other curing temperatures and times usable are 220° C for 20 min, 190° C for 60 min or 180° C for 120 min. If sticks of Araldite 1 are used, the surfaces must first be heated to 120° C, the stick rubbed over the surfaces and the curing operation undertaken as before.

Among the many examples of thermo-setting Araldite bonded seals, the following are typical. Roberts (R10) made vacuum-tight window seals of glass, fused silica, synthetic sapphire, fluorite or silver chloride within a thin copper diaphragm which could be cooled fairly rapidly to 77° K (liquid nitrogen boiling point) under vacuum and, in the cases of glass, synthetic sapphire and silver chloride, cooling to 20° K was possible. Thallium bromo-iodide window seals could be cooled very slowly to 77° K, and a synthetic sapphire disc sealed to Pyrex could be plunged into liquid nitrogen without damage. Schwarz (S11) used Araldite to seal windows of KBr to vacuum thermopiles within which the pressure had to remain below 10^{-3} torr for an unlimited time. Aluminium male cone-shaped electrodes are sealed by Araldite into the fitting female glass cones at the ends of the Leybold demonstration discharge tube. Kent (K8) used Araldite to seal glass tube to the refractory Mullite. Araldite Type 1 stick was applied in a thin layer to the warmed ends of the two tubes; the tube edges were placed together and temporarily held in place by springs during a curing process at 180° C for 1 hour in an electrically heated oven. Seals made with thermo-setting Araldite can withstand temperatures up to 150° C but prolonged use above this temperature causes gradual decomposition of the Araldite.

An ethoxylene resin Araldite 101 with hardener 951 sets at room temperature and has a low softening point. At temperatures above 60° C the bond strength decreases rapidly so that the members of the joint can be taken apart without damage to them. This material has been particularly useful in, for example, the assembly of the series of alternate ceramic and metal ring electrodes of the accelerator tubes for Van de Graaff generators (Miranda and Jones, MJ1). If a pressure of at least 15 lb/sq in. is applied to the joint during setting, tensile shear tests at 20° C for brass or steel specimens 1 in. wide with 1 in. overlap show that the bond strength is a maximum at about 0·75 ton/sq in. where the thickness of the adhesive is 0·001 in., indicating the machining tolerances permissible in the parts to be joined.

Demountable Seals

4.15. Vacuum Greases

A variety of greases with low vapour pressures are commercially available for application at room temperature to provide readily demountable seals between glass parts and, to a lesser extent, metals, particularly for cone joints, flat flange joints, ball and socket joints and stopcocks.

The chief types are the Apiezon greases and the silicone greases. The latter have remarkable constant viscosity characteristics over a wide temperature range but the viscosity at room temperature is higher than for the Apiezon products. Almost all the manufacturers of vacuum equipment supply vacuum greases, some of them under particular trade names. The vapour pressure at room temperature should not exceed 10^{-4} torr and is usually of the order of 10^{-6} torr.

4.16. Elastomer Seals

In vacuum plant, especially that made from metal, the most frequently used demountable joints employ elastomers for making the seal. Various natural and artificial rubbers are used but that most generally employed is Neoprene, which resists attack by oil. On the other hand, Neoprene cannot be heated to above 90° C because it acquires a permanent set whereas natural rubbers can be used up to 120° C. For higher temperatures up to 250° C silicone rubber can be used (*see also* § 4.25).

4.17. Rubber Gaskets and O-rings

A common type of seal is in the form of a gasket, usually ring-shaped though rectangular and other shapes are also used. The cross-section of the gasket may be circular (giving the so-called O-ring), square, rectangular or (for fitting over the open end of a glass bell-jar) of L-section (*see* Fig. 4.18).

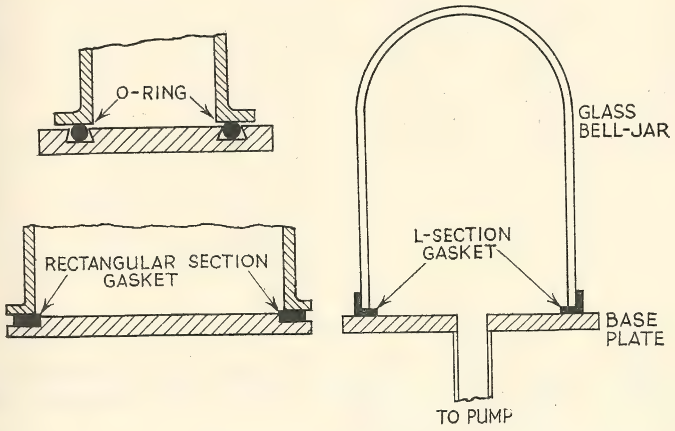


FIG. 4.18 Rubber gaskets

A cutter suitable for cutting gaskets of flat rectangular cross-section from rubber sheet is described by Allen, Mackle and Sutton (AMS1).

The design of vacuum plant has been especially facilitated by the use of O-ring seals which are generally moulded from extruded Neoprene and are available in several sizes from the vacuum equipment suppliers. Table 4.15 shows the extensive range available from Edwards High Vacuum Ltd. Those marked with an asterisk are in accordance with British Standard B.S.1806: 1951 and American Standard AN.6227.

TABLE 4.15
O-rings

No.	Internal diameter D,[1] inch[2]	Section diameter d,[1] inch[2]	No.	Internal diameter D,[1] inch[2]	Section diameter d,[1] inch[2]
VOR 101*	0·114	0·070	VOR 160*	2·225	0·210
VOR 2A	0·187	0·103	VOR 161	2·250	0·139
VOR 4A	0·312	0·103	VOR 164	2·375	0·139
VOR 104*	0·208	0·070	VOR 166*	2·475	0·210
VOR 105*	0·239	0·070	VOR 171	2·687	0·139
VOR 107*	0·301	0·070	VOR 179*	2·975	0·210
VOR 110*	0·364	0·070	VOR 182*	3·225	0·210
VOR 114	0·437	0·070	VOR 184*	3·475	0·210
VOR 116*	0·487	0·103	VOR 187	3·725	0·210
VOR 118*	0·549	0·103	VOR 190*	3·975	0·210
VOR 120*	0·612	0·103	VOR 194*	4·350	0·210
VOR 121	0·625	0·103	VOR 196*	4·475	0·275
VOR 122*	0·674	0·103	VOR 205*	4·975	0·275
VOR 124*	0·737	0·103	VOR 208	5·125	0·210
VOR 129*	0·859	0·139	VOR 213	5·375	0·210
VOR 130	0·875	0·103	VOR 214*	5·475	0·275
VOR 132	0·937	0·103	VOR 221	5·875	0·210
VOR 133*	0·984	0·139	VOR 222	5·975	0·275
VOR 135*	1·046	0·139	VOR 226	6·375	0·275
VOR 136*	1·109	0·139	VOR 227*	6·475	0·275
VOR 137	1·171	0·139	VOR 231	6·875	0·275
VOR 138*	1·234	0·139	VOR 232*	6·975	0·275
VOR 140*	1·359	0·139	VOR 236*	7·475	0·275
VOR 142*	1·484	0·139	VOR 237	7·625	0·275
VOR 146	1·625	0·139	VOR 240*	7·975	0·275
VOR 148*	1·725	0·210	VOR 242*	8·475	0·275
VOR 149	1·750	0·139	VOR 244*	8·975	0·275
VOR 154*	1·975	0·210	VOR 246*	9·475	0·275
VOR 155	2·000	0·139	VOR 248*	9·975	0·275
VOR 159	2·187	0·139	VOR 252*	10·975	0·275
			VOR 256*	11·975	0·275
			VOR 258*	12·975	0·275
			VOR 260*	13·975	0·275
			VOR 262*	14·975	0·275

[1] *See* Fig. 4.19.
[2] To convert to mm multiply by 25·4.

For larger diameters than those listed, a ring may be fashioned from extruded Neoprene cord which is scarf-jointed with self-vulcanizing cement (Fig. 4.19). Extruded cord is supplied with cross-sectional diameters of 0·500 in., 0·312 in. and 0·275 in.

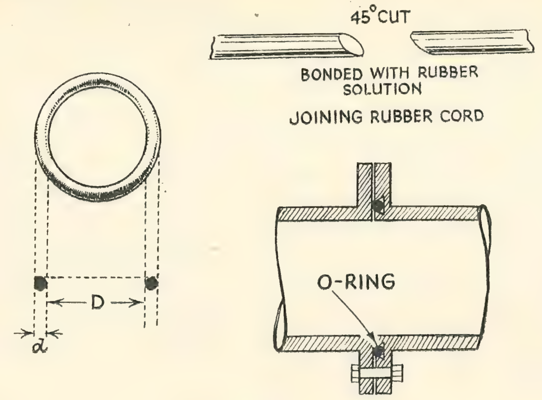


FIG. 4.19 O-rings

O-ring seals have been used in a considerable variety of ways but two chief applications are: (*a*) for seals between flat surfaces, *e.g.* a bell-jar with flat flange to a metal base-plate or between two flat flanges on metal tubes; (*b*) for making the seal around a metal or glass tube or rod inserted into a metal wall of a vacuum tank. The basic arrangement in case (*a*) is illustrated by Fig. 4.19. One of the flat surface metal members to be joined has a circular groove cut in it into which is inserted the O-ring. This groove may be of various forms: (1) the undercut, 'dovetail' type (Fig. 4.20(*a*)) which ensures positive

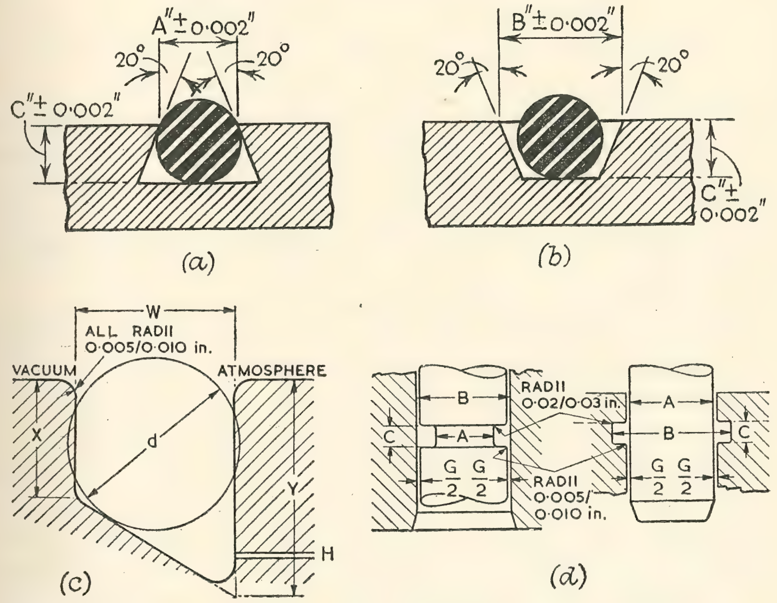


FIG. 4.20 O-ring seals

retention of the ring; (2) the more simply machined channel (Fig. 4.20(*b*)) in which the ring is loose; (3) the recently developed trapezium cut (Barton, B18) shown in Fig. 4.20(*c*). The last of these grooves has the advantages of straightforward machining, compression of the rubber ring without distortion, and enables the ready testing for leaks by a hydrogen probe method (§ 9.5) via the small drilled hole shown at H. Arrangements of O-rings suitable for sealing a rod or tube inserted into a wall of a vacuum plant are given by Edwards High Vacuum Ltd., and are illustrated by Fig. 4.20(*d*).

The machining of these grooves must be to dimensions to suit the particular O-ring. Reference to the arrangements illustrated in Fig. 4.20 in conjunction with Tables 4.16, 4.17 and 4.18 (based on data supplied by Edwards High Vacuum Ltd.) gives the correct dimensions. The internal diameter *D* of the ring should be such that it has to be stretched slightly to fit snugly in the groove; thus, the inside diameter of the groove should be 0·025 in. greater than the inside diameter *D* of the O-ring.

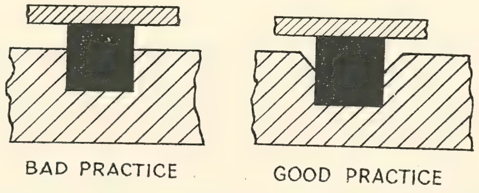


FIG. 4.21 Square section rubber gasket in channel

In the use of square or rectangular section rubber or Neoprene gaskets, the channel cut in the metal plate or flange should have bevelled edges to prevent undesirable extrusion or even cutting of the rubber at the corners. Good and bad practice (Guthrie and Wakerling, GW1) are illustrated in Fig. 4.21. Allowance must be made for 25 to 30% compression of the rubber under the mechanical load.

In the use of O-rings in general, a compressive force has to be applied to deform the cross-section of the ring to ensure a seal. If an O-ring is used to make a seal between flanges or between a flange and a flat plate and the internal diameter of the ring is more than 3 in., sufficient compression is achieved in suitable arrangements due to the atmospheric pressure alone. To ensure a seal, it is recommended that the compressive force on a Neoprene ring be at least 5 lb wt per inch length of the ring perimeter. Thus, a flat plate of metal or glass seated on an O-ring around a port-hole of diameter more than 2 in. in a flat wall of a vacuum tank or on a flat flange will provide adequate compression of the rubber due to the atmospheric pressure acting on one side of the plate. For smaller diameters, however, and in the assembly of vacuum plant involving unions between component parts like pipes, pumps, traps, valves, etc., of all diameters, but especially in positions where the compressive force due to the atmosphere does not come into play, some mechanical means of clamping together the surfaces bearing on the O-ring is essential. In providing such mechanical clamping, the rubber ring itself should not bear

All dimensions are in inches

TABLE 4.16

'Dovetail' groove dimensions (*see* Fig. 4.20(*a*) and (*b*))

Section diameter 'd' of O-ring	A	B	C
0·070	0·059	0·095	0·049
0·103	0·088	0·142	0·074
0·139	0·121	0·194	0·100
0·210	0·185	0·293	0·149
0·275	0·243	0·391	0·203
0·187	0·164	0·263	0·137
0·218	0·192	0·308	0·160
0·250	0·221	0·355	0·184
0·312	0·276	0·430	0·230
0·500	0·445	0·715	0·371

TABLE 4.17

Trapezium groove dimensions (*see* Fig. 4.20(*c*))

Section diameter 'd' of O-ring	W	X	Y
0·070	0·065	0·046	0·086
0·103	0·097	0·063	0·123
0·139	0·132	0·084	0·166
0·210	0·200	0·124	0·248
0·275	0·264	0·161	0·323
0·312	0·298	0·186	0·370
0·500	0·481	0·290	0·587

TABLE 4.18

Piston groove dimensions (*see* Fig. 4.20(*d*))

Section diameter 'd' of O-ring	(B–A)	C	G
0·070	0·112	0·078	0·005
0·103	0·165	0·112	0·005
0·139	0·224	0·150	0·006
0·210	0·340	0·223	0·007
0·275	0·448	0·270	0·008

any considerable load, the component metal parts should meet to bear the load with the rubber suitably compressed between them. The most usual means of clamping is by screw bolts through holes regularly spaced around the flanges between which the O-ring is placed (Fig. 4.22). Indeed, vacuum plant fabricated from metal is usually assembled by making joints of this kind between the various component parts.

O-rings are also much employed for making demountable seals and seals where one component can be moved in vacuum isolation valves and gas metering devices (Chapter 5). Apart from such applications, many reports in the literature and in the manufacturers' catalogues deal with the use of O-rings in particular applications. A survey of the more important of these follows.

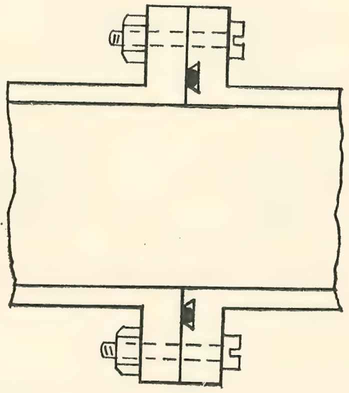


FIG. 4.22 O-ring bolted between metal flanges

4.18. Vacuum Pipe Connectors

Connectors based on O-rings of various designs are illustrated in Fig. 4.23. The best designs ensure that the rubber is not freely exposed to the vacuum. Kronberger (K7) recommends that identical metal flanges are brazed to the pipe in a jig by induction heating (Fig. 4.23(*a*)). For large and complex vacuum plants where leak-hunting is essential, a double O-ring seal is useful (Fig. 4.23(*b*)); indeed, the double O-ring can be a single moulding, the cross-section being dumb-bell shape. Before the assembly of such plant, each component is leak-tested. After assembly, but before the evacuation of the main volume, double O-ring joints can be leak-tested by evacuation of the small interspace volume between the O-rings via a suitable drilled hole and then determining the pressure rise on isolation. Moreover, when the plant is evacuated, search gas (§ 9.5) introduced to this interspace enables ready leak-testing of the joint.

Stiff (S12) has developed a simple method of connecting pipes based on his statement that any pipe (aluminium, brass, mild steel, stainless steel, copper) has merely to be machined flat on one end to be capable of being sealed by an O-ring to another pipe of the same diameter and configuration. However, an O-ring simply inserted between flat pipe ends would only be held between the mating surfaces by friction, so it is enclosed between two thin metal cylinders, one on the inside of the O-ring and inside the pipe, the other outside the pipe (Fig. 4.23(*c*)). To prevent the inside metal cylinder from sliding, a counterbore is machined in the pipe ends. This counterbore is dimensioned so that when the two pipes are clamped together they bear on the inside metal cylinder and squeeze the O-ring by the correct amount. The pipes are pulled together by loose clamping flanges pulling against the external wall of the pipes. The clamping is by six screw bolts. It is reported by Stiff that the O-ring can be of rubber, Neoprene, polyethylene, Teflon, copper or lead.

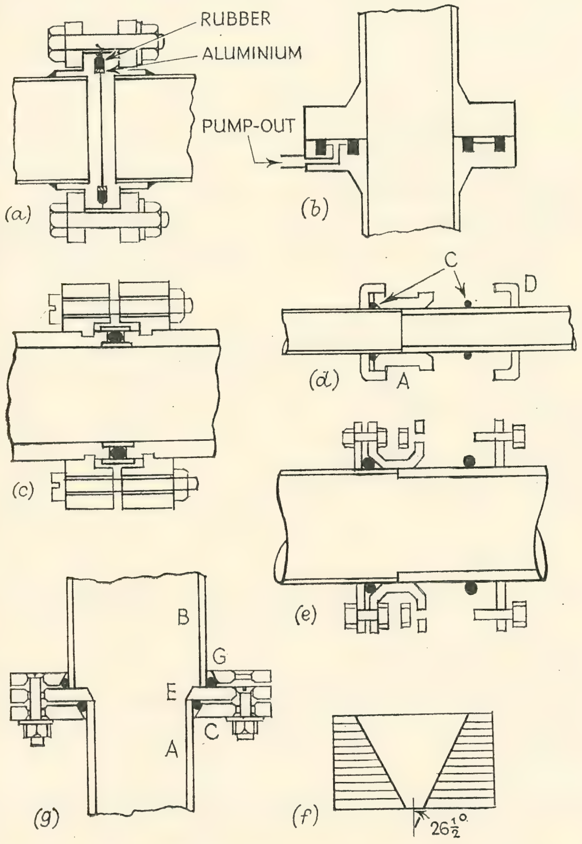


FIG. 4.23 Vacuum pipe connectors based on O-ring seals

Pollard (P6) also describes the use of O-rings for making readily assembled connections between metal pipes of the same diameter or between a metal and a glass pipe. A cylindrical metal body *A* (Fig. 4.23(*d*)) of bore diameter 0·005 in. to 0·01 in. greater than the outside diameter of the pipes to be joined has a 45° level at either end. An O-ring *C* is slipped over each pipe and compressed into the bevel by a threaded clamping ring *D* if the pipe diameter is $\frac{3}{8}$ in. to $1\frac{1}{2}$ in. and by a bolted flat clamping ring (Fig. 4.23(*e*)) for large-diameter pipes.

Garrod and Gross (GG1) have designed a set of easily machined metal discs containing central bevel-edged holes which can be used in conjunction with suitable O-rings to assemble quickly vacuum unions between different sizes of glass and/or metal pipes. The arrangement provides flexibility to permit self-alignment of the various elements of the vacuum system. The metal discs are each 2·5 in. outside diameter and 0·125 in. thick and are machined from duralumin rod (for lightness). Several of these discs are clamped together and eight equally spaced 6 B.A. clearance holes are drilled through them on a pitch circle of diameter $2\frac{1}{4}$ in. These holes are then countersunk on each side of each plate. Finally, the complete assembly of discs is clamped together and a conical hole of $26\frac{1}{2}°$ taper is bored through the unit, an angle which covers the range of sizes in steps of 0·125 in. (Fig. 4.23(*f*)). To construct a seal between two pipes *A* and *B* (Fig. 4.23(*g*)) one of the discs *E* of the unit is selected so that the smaller diameter pipe just sits on it. The O-ring of cord section diameter 0·125 in. is chosen so that, on stretching slightly, it slides over the pipe *A*. It is then clamped against the tube *A* and the disc *E* by a second disc *C* which is fastened to *E* by four bolts equally spaced around the circumference. A similar joint is made between disc *E* and the second pipe *B* by a third disc *G* with an O-ring.

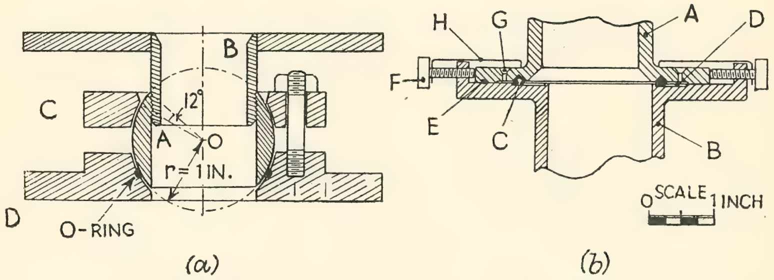


FIG. 4.24 Vacuum pipe connectors based on O-ring seals and in which movement is possible

Lee and Young (LY2) describe a joint of large conductance between two sections where movement of one section through a few degrees in any direction with respect to the other is made possible by the use of an O-ring and spherical metal member (Fig. 4.24(*a*)). This joint provides a similar facility of movement to metal bellows, but with the advantages of more degrees of freedom and ready ability to clamp in the desired position. The part *A* of this joint is machined from solid brass, the spherical surface being fashioned after the boring and screw-cutting. Tube *B* is threaded into the bore of the sphere *A* and soft-soldered from inside the sphere. The ring *C* and the flange *D* have inner concave spherical surfaces of the same radius as *A*, and the vacuum seal is made by a greased O-ring in a groove cut in *D*. For the dimensions given in Fig. 4.24(*a*), the O-ring used has an internal diameter of 1·812 in. This type of joint was used in the alignment of the target system in a nuclear particle accelerator experiment.

Garrod (G6) has used an O-ring to make a seal between two metallic flanged cylinders *A* and *B* and where, by means of screws, relative translation between the cylinders in a plane normal to their axes is possible. In the flange of the cylinder *A* (Fig. 4.24(*b*)) is machined a circular V-section groove into which is fitted the Neoprene O-ring *C*. The flange on cylinder *B* contains a shallow trough *D* of such a depth that the two flanges come into contact over the area *E* when the gasket is compressed by approximately 7% of its section diameter. The mechanical load on the gasket is thus restricted. The trough and the mating metal surfaces at *E* are lightly coated by application at *G* of a mixture of silicone grease or oil and graphite (1 part of graphite to 10–15 parts of oil) to provide lubrication. Four push screws, such as *F*, enable translatory movement to be imparted in two directions. With a suitable mechanical contrivance, isolation of one member relative to the other is also possible. For small diameter pipes, extra compressive force is provided by a compression spring.

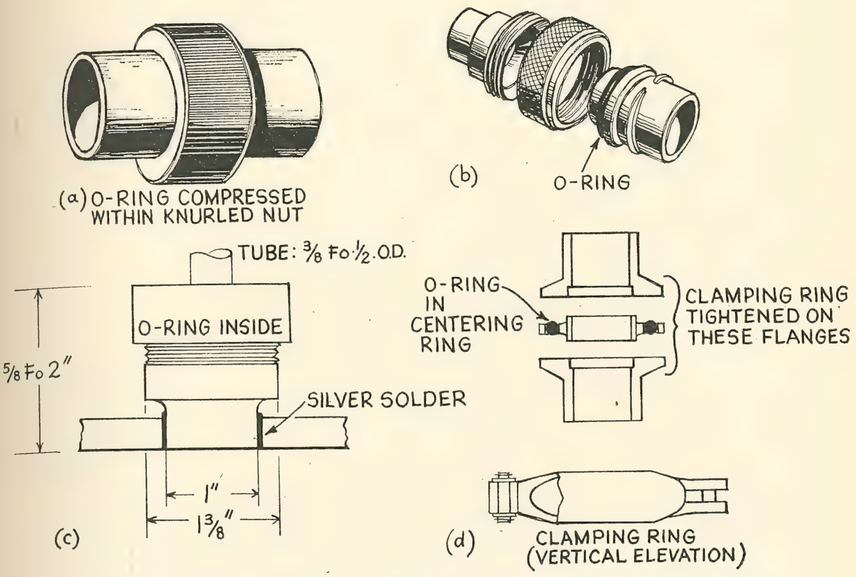

(a) O-RING COMPRESSED WITHIN KNURLED NUT
(b)
O-RING
TUBE: 3/8 to 1/2 O.D.
O-RING INSIDE
1 5/8 to 2"
SILVER SOLDER
1"
1 3/8"
(c)
O-RING IN CENTERING RING
CLAMPING RING TIGHTENED ON THESE FLANGES
(d)
CLAMPING RING (VERTICAL ELEVATION)

FIG. 4.25 Vacuum connectors based on O-ring seals marketed by various manufacturers

(*a*) *Central Scientific Company, U.S.A.*
(*b*) *Edwards High Vacuum Ltd., Britain*
(*c*) *National Research Corporation, U.S.A.* (and *Vacuum Industrial Applications Ltd., Britain*)
(*d*) *E. Leybold's Nachfolger, Germany*

In Fig. 4.25 are shown a variety of vacuum connectors based on O-ring seals which are commercially available.

4.19. End-plate Seals

Such seals, based on O-rings, are particularly useful for demountable vacuum plant such as that used for experimental work in electron-optics. A usual arrangement is a glass or metal cylinder arranged horizontally and provided with flat end cover plates through which lead-in terminals may be provided.

The authors have used an arrangement with ring-shaped aluminium end-pieces sealed to each end of a cylindrical glass tube by means of W-wax. Dovetail grooves in the flat flanges so provided retain O-rings against which the end plates of metal or glass can be placed and held in position when the cylinder is evacuated (Fig. 4.26(*a*)). Alternatively, the dovetail groove containing an O-ring can be in the cover plate and this held against a flat flange on the glass or metal cylinder. A simpler method (Smith, S13) is to support the O-ring on a fitting inner metal ring and place it between the cylinder flange and the cover plate (Fig. 4.26(*b*)). Richards and Smith (RS1) point out that flanges on the cylinder ends forbid the insertion over the tube of close-fitting magnetic focusing and screening coils which may be used in electron-optical studies. To avoid these flanges, they have used the arrangement shown in Fig. 4.26(*c*) whilst Fig. 4.26(*d*) illustrates a more complex assembly which will carry seven lead-in terminals.

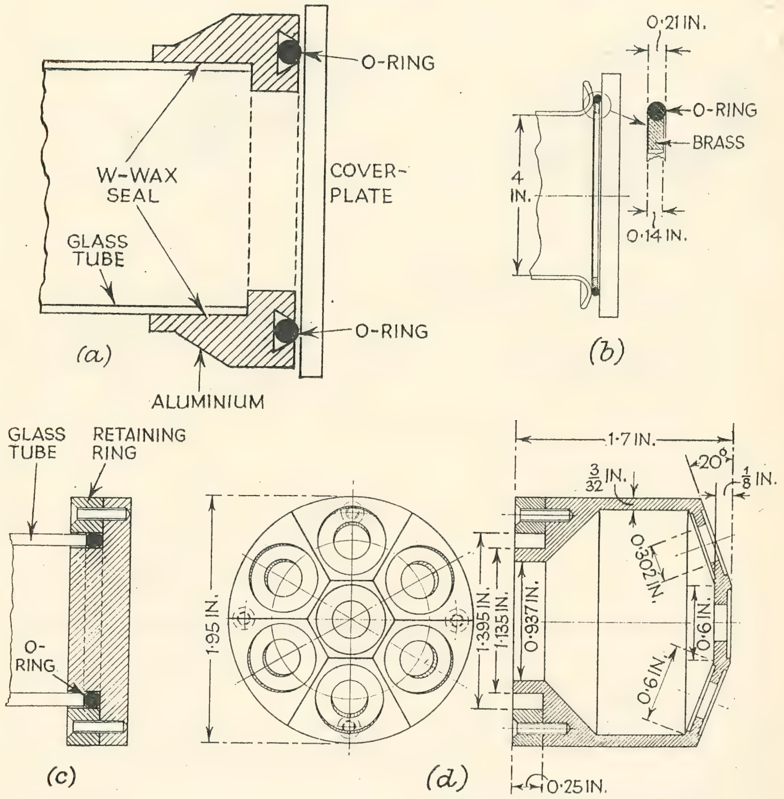

0·21 IN.
O-RING
O-RING
BRASS
W-WAX SEAL
COVER-PLATE
4 IN.
0·14 IN.
GLASS TUBE
O-RING
(a)
(b)
ALUMINIUM
GLASS TUBE
RETAINING RING
O-RING
1·7 IN.
3/32 IN.
20°
1/8 IN.
0·302 IN.
1·95 IN.
1·395 IN.
1·135 IN.
0·937 IN.
0·6 IN.
0·6 IN.
(c)
(d)
0·25 IN.

FIG. 4.26 The use of O-rings to provide a seal between a cylinder and an end cover plate

4.20. Lead-in Seals

Lead-in seals based on O-rings and rubber washers have been developed for providing current-carrying electrodes and for the insertion of metal or glass tubes into the wall of a vacuum system. Figure 4.27 illustrates various electric lead-ins available commercially (*see also* Fig. 4.20(*d*)). An insulated electric lead-in described by Edwards (E4) which is easily demountable and with a minimum of Neoprene exposed to the vacuum is shown in Fig. 4.27(*e*); this was developed for a current lead-in able to carry 325 amp for a vacuum furnace. A simple arrangement which can be constructed in a wide variety of sizes is due to Hayward (H14) and is shown in Fig. 4.27(*f*). For small currents and insulation resistances up to $10^5\Omega$, glass-bead seals are often used (*see* Fig. 4.10).

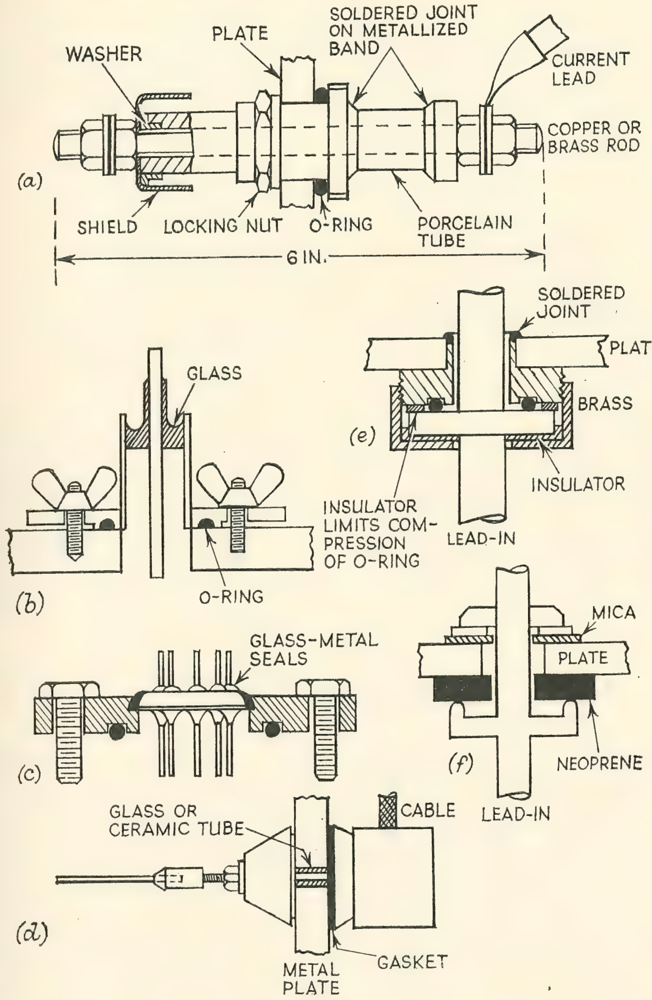

WASHER
PLATE
SOLDERED JOINT ON METALLIZED BAND
CURRENT LEAD
COPPER OR BRASS ROD
(a)
SHIELD
LOCKING NUT
O-RING
PORCELAIN TUBE
6 IN.
SOLDERED JOINT
PLATE
GLASS
BRASS
(e)
INSULATOR
INSULATOR LIMITS COMPRESSION OF O-RING
LEAD-IN
(b)
O-RING
MICA
GLASS-METAL SEALS
PLATE
(c)
(f)
NEOPRENE
GLASS OR CERAMIC TUBE
CABLE
LEAD-IN
(d)
GASKET
METAL PLATE

FIG. 4.27 Vacuum electric lead-ins

4.21. Rotary Vacuum Seals

Seals of this type based on O-rings are illustrated in Fig. 4.28. Some of these also enable a translatory motion to be imparted to the entering rod or tube. The O-rings used must be lubricated by a low vapour pressure grease or oil, the latter being preferred. The use of two separated O-rings which enclose between them an oil seal (Fig. 4.28(*c*)) is particularly attractive especially if the shaft is rotated continuously by a motor drive (*see also* § 4.24). Sikorski and Woods (SW1) describe a rotatable seal (made by Flexibox Ltd.) consisting of two flat collars pressed together by a spring. One collar 1 is made of compounded carbon (Fig. 4.28(*d*)) and is held stationary and sealed to the cover *C*, mounted on the body *B* of the vacuum chamber, by a Neoprene O-ring 2. The other collar 5 is of stainless steel and is a clearance fit on the rotatable shaft *A* to which it is sealed by the rubber ring 6. The stainless steel spring 7 is an interference fit on the shaft at one end and on the neck of ring 5 at the other. Rotation of the shaft tends to increase the grip of the spring on these two members. This spring is under compression and hence presses the collars together and also rotates collar 5 with the shaft without strain on the sealing Neoprene O-ring 6. Improvement of the seal and lubrication are provided by Apiezon B oil between the shaft *A* and the cover *C*. If it is required to cool the seal, water channels are provided in *C*. It is reported that a shaft of 1 in. dia can be rotated at speeds of 600 to 900 r.p.m. whilst a pressure of 2×10^{-4} torr is maintained indefinitely in a 1·5 litre chamber by an oil diffusion pump with a speed of 30 litre/sec. Inversion of this seal so that the atmospheric pressure increases the pressure between the sliding rings and also the oil in the seal is at atmospheric pressure instead of inside the vacuum chamber, should give considerable improvement but has not yet been tried.

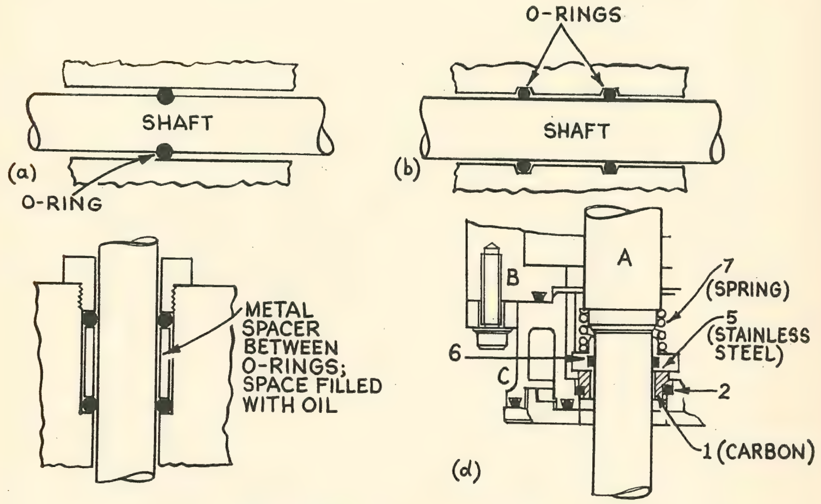


FIG. 4.28 Rotary vacuum seals

4.22. Rectangular Rubber Gaskets

These require particular attention to the design of the channel to take the gasket because of the difficulty of fitting-in at the corners. Figure 4.29 illustrates the usual arrangements (Guthrie and Wakerling, GW1).

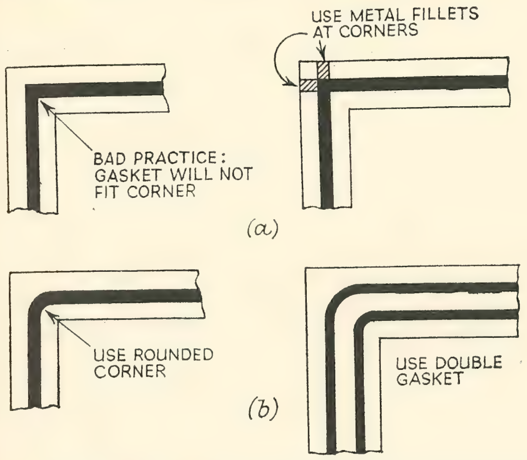

USE METAL FILLETS AT CORNERS
BAD PRACTICE: GASKET WILL NOT FIT CORNER
(a)
USE ROUNDED CORNER
USE DOUBLE GASKET
(b)

FIG. 4.29 Corner of rectangular channel in metal plate containing rubber gasket

In Fig. 4.29(*a*) straight channels are milled in the metal to the edge, metal fillets are welded in position and the surfaces then ground smooth. For gaskets of section width less than 0·125 in., the corners of the rectangular channel may be rounded as shown in Fig. 4.29(*b*), but then the milling is difficult.

4.23. Gaskets Supported by Metal Inserts

The use of elastomer gaskets without special groove cutting is attractive. A specially shaped metal ring within the gasket facilitates this (*see*, for example, Fig. 4.26(*b*)). Metal rings with cemented-on gaskets are used for pipe-connectors and in air-admittance valves. Samuel (S14) has designed grooveless gaskets of up to 6 in. dia in which rubber is vulcanized to both sides of a

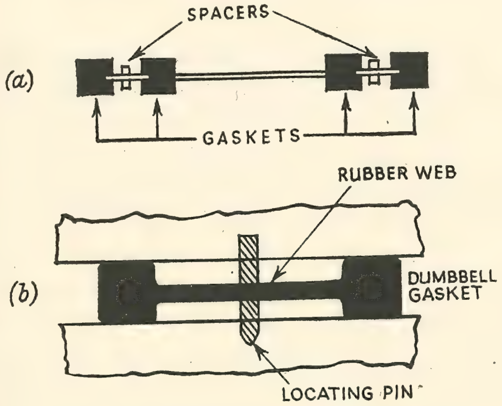


FIG. 4.30 Grooveless gaskets (*Samuel*)

metal ring which may be used on standard flanges (Fig. 4.30(*a*)). The dumb-bell gasket (Fig. 4.30(*b*)) may also be used without specially cut channels in the mating metal surfaces.

4.24. The Wilson Seal and the Gaco Seal

The Wilson seal (Wilson, W3) is especially useful in cases where a sliding or rotary motion is to be imparted to a shaft or tube entering the wall of a vacuum system. Three designs are illustrated in Fig. 4.31: (*a*) in which a single Neoprene washer is used; (*b*) in which two Neoprene washers are employed and a pump-out drill hole enables the space between the two to be evacuated to reduce air leakage; (*c*) a design suitable for a glass plate (Smith, S13).

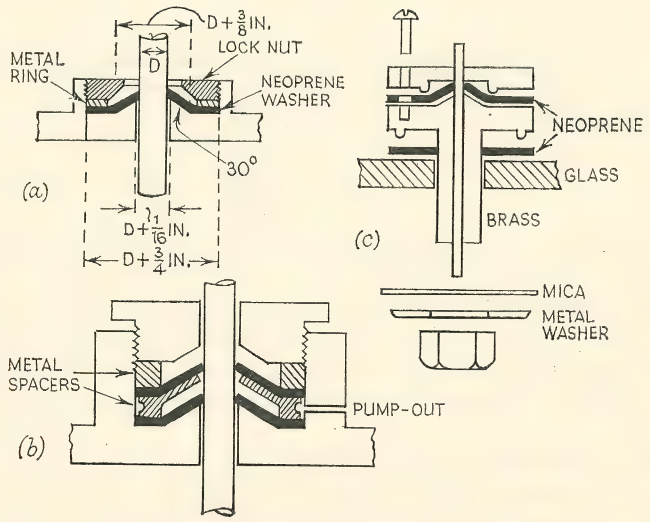


FIG. 4.31 Wilson seals

In the Wilson seal, the hole pierced through the centre of the rubber washer is approximately two-thirds of the shaft diameter, and this washer is flexed at the centre by the 30° conical bevel on the metal plate. The seal against the shaft is due to the 'snap' of the curved washer rather than to the compression under atmospheric pressure (Dawton, D7). Indeed, for this reason, the seal can be employed the wrong way round. To ensure satisfactory performance the shaft surface must be polished smooth, the gasket must fit well in the gland, and the gasket hole must have clean, smooth edges and be lubricated by a slight amount of vacuum grease. If the seal has to withstand temperatures of about 100° C, Dawton (D7) recommends the use of a metal spring over the rubber washer to assist its 'snap' against the shaft. Wilson seals can be used with shaft diameters from $\frac{1}{16}$ to 1 in.; larger sizes can be employed, but it must be ensured that the pressure of the atmosphere does not force the shaft into the vacuum. The design with two Wilson washers can have the space between filled with oil to provide lubrication and extra precaution against air leaks.

Hayward (H14) describes two modified forms of Wilson seal in which accurate shaping of the rubber gasket is unnecessary. A simple rotary seal (Fig. 4.32(*a*)), suitable for light duty, has a rim on the shaft *B*, *C* and *D* being machined in one piece and hard-soldered to the shaft. The Neoprene washer *E* is held in place by a screwed nut *F* provided with a lock-nut *G*. The face of the body *A* on which the Neoprene rests has a raised ring to ensure a better seal. It is also essential for the top of the rim *C* to be above the top of the body *A* to ensure a good seal between the rim and the Neoprene. For a shaft diameter of $\frac{3}{16}$ in. the rim diameter should be about $\frac{5}{16}$ in. and the overall diameter $\frac{3}{4}$ in. It is, however, difficult to lubricate this type of seal satisfactorily for continuous operation. A second seal (Fig. 4.32(*b*)) for continuous rotation has a similar body *X*. At the bottom of the cup is a hardened steel washer *Y* and the shaft *Z* has a disc hard-soldered to it. A triangular rim *R* (instead of a circular rim) is soldered on the top side of this disc whilst the underside contains three shallow holes arranged symmetrically about the shaft axis and each carrying steel balls which bear on the bottom steel washer *Y*. The triangular rim is packed with Apiezon grease which is distributed over the undersurface of the Neoprene during rotation.

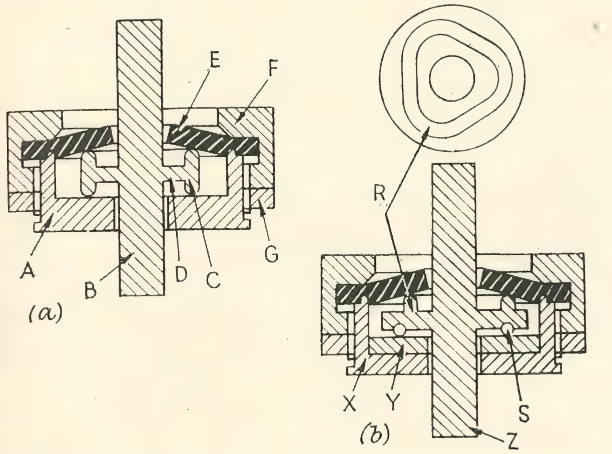


FIG. 4.32 Modified forms of the Wilson seal (*Hayward*)

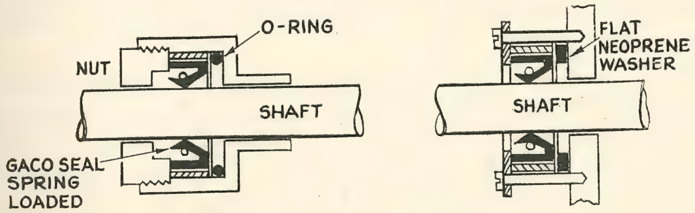


FIG. 4.33 Gaco seals

Two arrangements of the spring-loaded Gaco seal (a product of G. Angus and Co. Ltd.) are illustrated in Fig. 4.33.

Various reports have appeared in the literature on the rate at which gas flows through elastomer seals and their outgassing. It is difficult to give consistent data owing to the variation in conditions from one type of experiment to another. Dawton (D7) has made tests on rotatable shaft seals using Neoprene lubricated with Apiezon B oil (preferred to a vacuum grease) of the Wilson and Gaco types and reports that, at room temperature, there is little difference between the leakage rates of the various modifications. The term leakage is used here, although most of it is due to condensable vapour (of unknown composition) from the Neoprene and also, most likely, due to moisture deposited on the shaft and lubricant on exposure to air and then, on movement of the shaft, introduced into the vacuum. For a static shaft of diameter $\frac{3}{8}$ in., the leakage rate as determined by the rate of pressure rise recorded on a Pirani gauge (without liquid air on the vacuum system) was about $1{\cdot}2 \times 10^{-3}$ l.μ/sec after eight hours pumping. Rotation of the shaft at 1 r.p.s. increased the leakage rate threefold. For a reciprocating in-and-out motion of the shaft, the leakage was found to be proportional to the distance the shaft moved and independent of the speed of motion if less than 4 cm/sec, but increased with greater speeds. The leak on the in-motion of the shaft was about six times that on the out-motion. This suggests that the chief cause of leakage is the lubricant which enters the vacuum system with the shaft; indeed, the use of a thicker lubricant resulted in increased leakage. If a liquid-air filled trap were used on the system, the apparent leakage rate was reduced to about 10%, indicating that some 90% of the leakage is condensable vapour and may well originate from the lubricant. The omission of the lubricant made it impossible to move the shaft if rubber washers were used, though some movement was possible using Neoprene, but it caused distortion of the washer.

To ensure low leakage in a Wilson or Gaco seal, Dawton emphasizes that the hole in the washer must be round, smooth and with squarely cut edges, with a Shore hardness of 50 to 55 for a Wilson seal and about 85 for a Gaco type. The shaft surface must be smooth and free from markings, especially circumferential ones. Shafts of glass, steel and brass all gave similar leakage rates. The shaft should have its end tapered for about $\frac{1}{8}$ in. to allow ready insertion in the washer.

Tests at 120° C showed that failure began after heating for two days, except for spring-loaded seals. Neoprene lubricated with DC 702 silicone oil appeared to last longer than other combinations. Spring-loading of the seal resulted in a much improved performance: heating at 120° C for 100 to 200 hours without failure was possible, though more frequent lubrication was necessary than when operating at room temperature. The simplest and most satisfactory seal was the Gaco type (Fig. 4.33), though when used at 100° C it was often necessary to tighten the housing screws which became loose on cooling.

Neoprene is alleged to have about $\frac{1}{10}$ of the gas permeability of natural rubber.

4.25. Silicone Rubber Gaskets

The use of silicone rubbers affords the advantage that heating to about 250° C is possible. The chief disadvantages are that silicone rubber is liable to take up a permanent set on compression, that it is considerably more expensive than Neoprene, and that it has a higher permeation rate to air than natural rubber. Gale and Machin (GM1) emphasize that the seal must be carefully designed because of the high linear thermal expansion coefficient of about 250×10^{-6} per °C, the small compressibility (less than for water) and the permanent set acquired on compression. The groove design must consequently provide sufficient space for expansion of the gasket without appreciable deformation. Three types of groove recommended by Gale and Machin are illustrated in Fig. 4.34. These workers used rings with an internal diameter of 4·375 in. and a square cross-section of 0·237 × 0·237 in. (6 × 6 mm) moulded from Silastic 160 (Dow Corning Corporation) by the Dunlop Rubber Company. The spigot in the upper seal was arranged so that the maximum deformation of the ring at room temperature was only 10% of its natural thickness and was shaped so that at 150° C the minimum thickness of the ring was not less than 0·75 of its maximum value. Permanent set resulted from any greater compression.

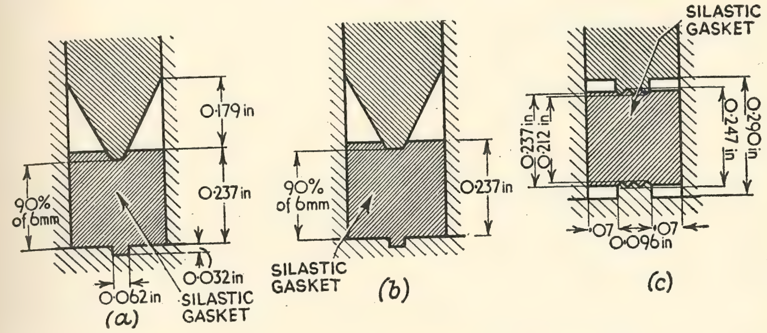


FIG. 4.34 Grooves for silicone rubber gaskets

Silicone rubbers have a higher permeation rate to air than Neoprene and natural rubbers; after a bake of one hour at 150° C and then cooling, Gale and Machin report that the gaskets have a leak rate of 0·07 l.μ/sec, alleged to be primarily through the material and not due to any imperfection of the metal-silicone junction. Slight permanent set was obtained; as a result, breaking of the joint and then re-making caused the leak-rate at room temperature to be doubled, but the lower rate was regained on baking. Recovery from permanent set is likely on standing for a few months. With adequate pumping, pressures of 10^{-4} torr could be attained in systems using the gaskets.

4.26. Teflon Gaskets

Teflon is the trade name for the plastic polytetrafluoroethylene (I.C.I. Plastics Division Ltd.). It can be used over the temperature range from −190° C to 280° C, is a good insulator and is chemically resistant to many organic liquids, to hydrofluoric, sulphuric and nitric acids and to alkalis. It is readily machined at high cutting speeds, soap solution being a suitable lubricant. Its vapour pressure at 25° C is 10^{-6} torr and at 350° C it is 3×10^{-5}

torr. It withstands weathering over very long periods. The dynamic coefficient of friction of Teflon against steel is only 0·03 to 0·1. It is therefore an attractive material for use as a gasket in rotatable shaft vacuum seals in that a lubricating oil is unnecessary. As a gasket material it suffers from plastic deformation under load. To overcome this difficulty, the thickness of the gasket is reduced to take advantage of the constraint at the clamping surfaces. The specially shaped Teflon washer shown in Fig. 4.35(*a*) has been used by the authors in

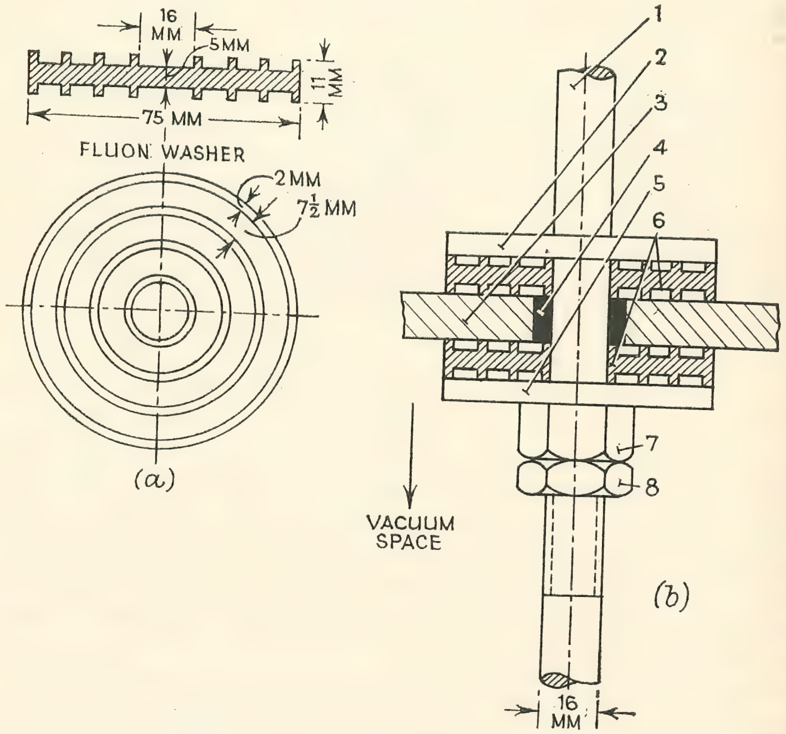


FIG. 4.35

(*a*) A Teflon washer

(*b*) High voltage lead-in using Teflon washer

1, Brass or copper electrode; 2, fixed collar (brass or copper); 3, wall of the container; 4, rubber insulating ring; 5, brass or copper ring; 6, two Teflon or Fluon washers; 7, nut; 8, locking nut

a high-voltage lead-in of the design illustrated by Fig. 4.35(*b*). The ribbing on the Teflon washer enables high constraint to be obtained on the metal clamping surfaces. Giaimo (G7) has designed a ring-type Teflon gasket which can be used up to 100° C. It utilizes a Teflon disc 0·226 in. thick and 1·745 in. o.d. with a 1 in. dia hole which was machined to a U-shaped cross-section of thickness 0·02 in. with the open end of the U facing outwards in the horizontal plane (Fig. 4.36).

A closely-wound helical spring with a coil diameter of 0·185 in. wound from piano wire of 0·01 in. dia was laid loosely in the U and sealing was accomplished by compressing the gasket between two surfaces inclined at 35° to the normal, so producing a radial as well as an axial compressive force. Therefore, when used as a gasket in a rotatable shaft vacuum seal, the Teflon shell was pushed against the shaft passing through the gasket centre. It is alleged that the Teflon returns to its original shape when released, and can therefore be re-used.

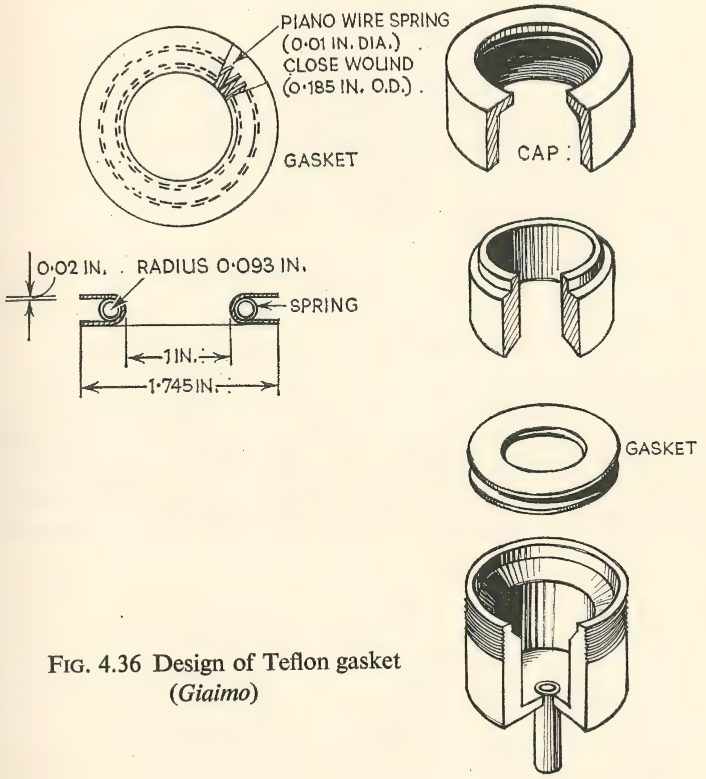


FIG. 4.36 Design of Teflon gasket (*Giaimo*)

Billett and Bishop (BB3) have devised a rotatable shaft vacuum seal using thin Teflon washers interspaced with metal washers to give good flow conditions under the mechanical pressure applied to four screws by a standard Allen key (Fig. 4.37).

Four Teflon washers, each 0·062 in. thick, were used. These were a tight push-fit on the shaft and to the walls of the recess cut in the metal wall of the vacuum chamber. The metal washers were of the same thickness (though this is not critical) and were highly polished to ensure good flow conditions for the Teflon. The clearance between the metal washers and the shaft was 0·01 in., providing space for flow of the Teflon. This device worked satisfactorily at temperatures between 20° and 200° C with a leakage rate less than 10^{-8} litre-torr per sec.

Davies (D8) alleges that Teflon seals are unreliable at temperatures approaching 300° C, even if the Teflon thickness is only 0·005 in. He has therefore used instead a diaphragm seal made of flat spring steel 0·005 in. thick, free from surface defects, and coated with Teflon (Fig. 4.38). The uniformly thick steel, free from surface defects, is cleaned on both sides by fine emery paper and then cathodically at a current density sufficient to cause vigorous degassing in a saturated solution of caustic soda in technical methanol. The disc is then washed in tap water to leave a hydrophilic surface and is then immersed, whilst wet, in an aqueous dispersion of Teflon (Teflon Dispersion, Teflon 30, from the *Laboratory Apparatus and Glassblowing Company, Manchester*). The coated disc is then spun at about 500 r.p.m. to throw off surplus dispersion and leave an evenly thin film. This is dried by radiation from a lamp and then sintered by playing a soft Bunsen flame on the rotating disc until the surface appearance changes from 'milky' to transparent. Ample, well-distributed clamping of the diaphragm between stainless steel flanges bolted together is essential. The seals are at first imperfect, but heating at about 300° C renders them vacuum-tight; subsequently they may be cooled and re-heated frequently without deterioration.

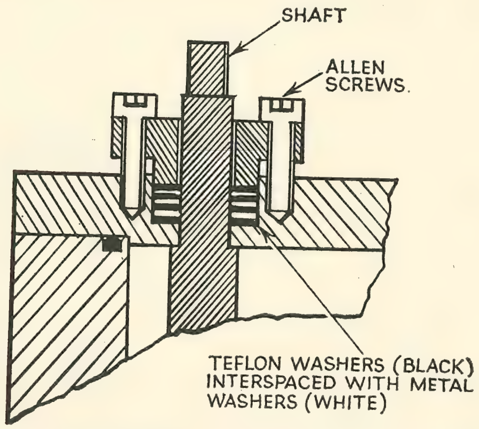

SHAFT
ALLEN SCREWS
TEFLON WASHERS (BLACK) INTERSPACED WITH METAL WASHERS (WHITE)

FIG. 4.37 Teflon gasket vacuum seal (*Billett and Bishop*)

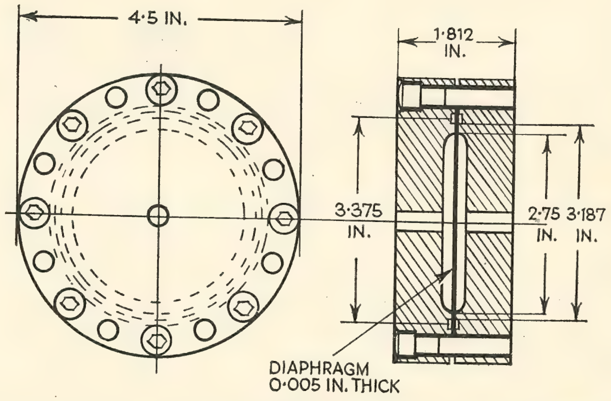


FIG. 4.38 A Teflon-coated thin steel diaphragm seal for temperatures up to 300° C

4.27. Metal Gaskets

The advantages of metal gaskets compared with those of rubber or Neoprene are (1) the outgassing is much less (2) the vacuum system can be thoroughly degassed by baking at temperatures well above those possible with even silicone rubber. Indeed, a design problem which remains to be solved is that of a demountable vacuum plant in which residual gas pressures as low as 10^{-7} torr or even less can be maintained. With Neoprene gaskets and without a degassing bake, it is difficult to attain less than 5×10^{-6} torr in well-designed plant. The use of gaskets of plastic metals assists in this aim, though no solution is yet available of problems such as those encountered in electron microscopy of providing vacuum seals through which shafts and the like can be repeatedly subjected to translatory and rotary motions and where the gas pressure is less than 10^{-6} torr.

Lead wire gaskets have been used to a small extent for many years. Recently, ring-shaped gaskets of copper and aluminium have been increasingly used, and also gold, silver and indium in special applications. Indeed, aluminium O-rings of circular cross-section are employed in some cases in place of Neoprene ones for seals between vapour pumps and the header.

The chief difficulties with metal gaskets are: (1) gas leaks which can only be minimized by ample clamping of the gasket between heavy flanges and by ensuring that the gasket is free from surface defects, particularly scratches, *even those invisible to the naked eye* and only shown up by a magnifying glass; (2) the design of an arrangement which is satisfactorily leak-free at elevated temperatures; (3) though a seal with low leakage may be produced, it is not always possible to dismantle and reassemble the seal repeatedly and yet retain vacuum tightness.

Kronberger (K7) has published a design of a copper ring seal between stainless steel flanges at the junction between pipes to carry liquid sodium and which is reported to remain vacuum tight with repeated heating up to 200° C (Fig. 4.39(*a*)). Martin (M8) recommends that for permanent connections the best seal is made from 25 S.W.G. aluminium sheet bolted between two flanges, one flat and the other having a raised ridge 0·02 × 0·01 in. On a 12-in. dia chamber, the leakage rate of such a seal was 0·007 l.μ/sec at room temperature. This writer also alleges that seamless wire rings of aluminium and copper (available commercially) give good seals in the conventional O-ring grooves. All seals were satisfactory down to liquid air temperature; aluminium seals could be heated to 400° C whilst copper ones could be heated to 800° C, though the leakage rates rose slightly with temperature. These seals would presumably demand very ample clamping between flanges. Martin has also used successfully for demountable seals at room temperature, wire rings of indium in hand-tightened pipe unions or clamped between flat flanges; and mentions also solid mercury seals where the mercury is frozen in an O-ring groove by a surrounding container filled with solid carbon dioxide or liquid air.

Holden, Holland and Laurenson (HHL1), also Elsworth, Holland and Laurenson (EHL1) have used successfully an aluminium wire (22 S.W.G.) gasket between flat steel flanges. Super-purity (99·99%) aluminium wire was used; the ends of the wire were butt-welded to form an endless loop. Provided the gasket was highly compressed by bolting together the steel flanges on either side of it, baking the seal at temperatures up to 550° C was permissible. On baking the seal to temperatures above 400° C, the aluminium flowed plastically and adhered to the flanges.

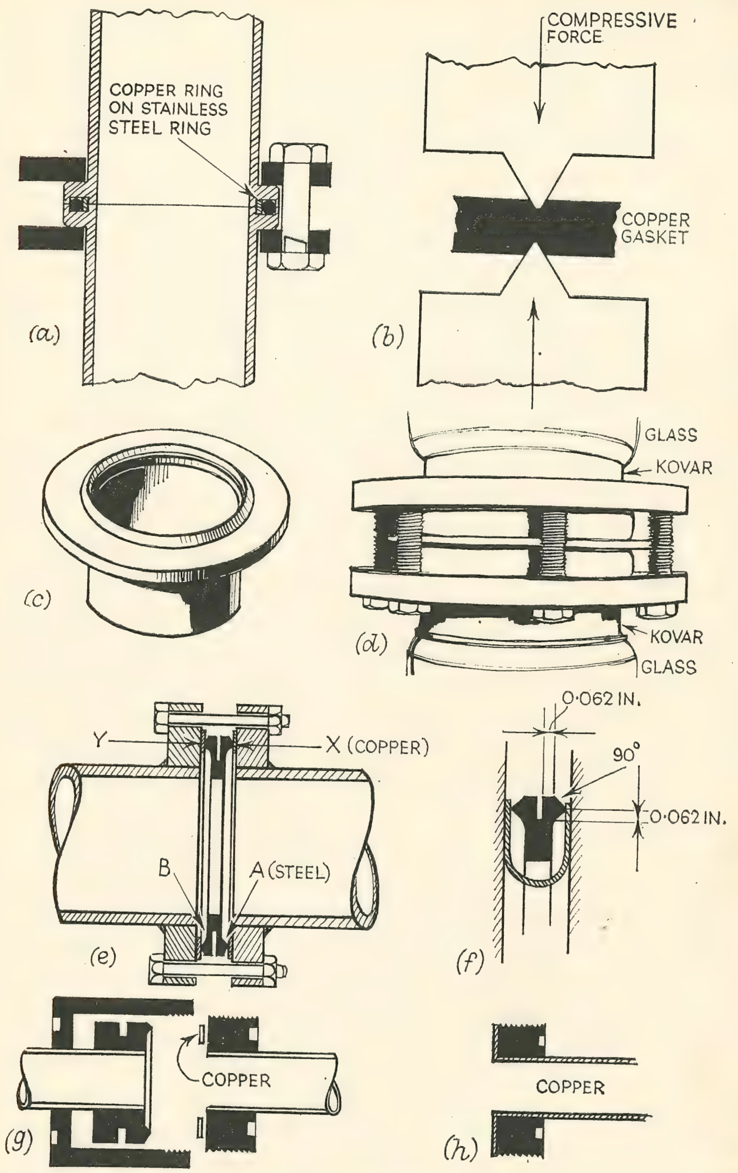


FIG. 4.39 Metal gaskets

Hees, Eaton and Lech (HEL1) stress the virtues of the knife edge vacuum seal (Fig. 4.39(*b*)), using a soft commercial copper flat ring gasket. This type of seal, of diameters ½ in. to 12 in., is reported to be 'absolutely tight', and has been used on liquid nitrogen traps as well as for joints cycled repeatedly from 25° to 400° C, and is able to contain 'vacua of approximately 10^{-10} torr for extended periods of time'. The profile of the knife edge used on the clamping members is shown in Fig. 4.39(*c*). The land of the knife edge is flat over a width of 0·003 to 0·007 in. The diameters of the mating knife edges must be the same with the knife edges in line. A wider flat land on the knife edge may be used but greater compressive force is then required. The compressive force must be obtained from a device (usually bolts) under stress, but not to a degree beyond its elastic limit so that minor dimensional changes (as when heated) may be permitted. The surface finish of the knife edge is not considered to be critical; this statement seems to be unjustified, especially as surface scratches should surely be removed as far as possible. In clamping the metal gasket between the knife edges on the flanges, an appropriate tightening sequence is important; if the bolt holes are too slack a fit to ensure alignment of the knife edges, guide pins must be inserted. The material of the knife edge must be harder than that of the gasket and, on clamping, bite into the gasket to a depth of 0·002 to 0·010 in.

Flanges of low carbon steel and stainless steel with machined or lapped knife edges have been used with soft copper, soft aluminium and also nickel gaskets of thickness $\frac{1}{16}$ in. In addition, knife edges of Kovar, ceramics, quartz and sapphire have been tested. The gaskets can be re-used several times, but it then becomes increasingly more difficult to make a satisfactory seal.

A number of different seals using knife edges are described by Hees, Eaton and Lech. A 1·5 in. dia seal developed to join glass to glass was much used (Fig. 4.39(*d*)). These employ glass tube to a length of Kovar of wall thickness 0·03 in. The length (½ in. to 1 in.) of the Kovar must be carefully considered in relation to the type of steel used for the knife edge, otherwise the difference in the thermal expansion between the two metals causes excessive strain on the metal-to-glass seal. The compressive force is applied by means of bolted flanges. These seals have withstood 48 bakes at 400° C for 1 hour. They have proved useful in the quick assembly of static, glass vacuum systems, where flexible metal bellows were used in the piping at appropriate places to facilitate alignment. Other applications of the knife edge seal described are in a liquid nitrogen trap, an ionization gauge, and for a vacuum furnace in which the large top cover plate is sealed in this way and, furthermore, ceramic knife edge seals are used for one pair of the heater leads which must be insulated from the surrounding metal flange.

Robinson (R11) describes a 4-in. dia metal seal which allows flat flanges to be joined. Two flat ring copper washers X and Y, each 0·01 in. thick (Fig. 4.39(*e*)), are used to make the seal—these must be particularly free from surface scratches, especially radial ones. These are placed on the polished flat steel or copper flanges on the pipes to be joined and between them is sandwiched a steel ring on which two annular knife edges *A* and *B* are turned.

A narrow slot is cut into the centre of the periphery of this steel ring so that when the flanges are bolted together there is a cantilever action on the knife edges. This system of knife edges must be stiff enough to ensure adequate 'bite' into the copper washers, both at room temperature and when the joint is baked to 450° C. Six equi-spaced bolts around the flanges provide the compressive force required. A single U-section copper washer (Fig. 4.39(*f*)) may be used as an alternative to the two single washers. Another application using a single flat copper washer is the joining of two small diameter pump lines (Fig. 4.39(*g*)). Using copper tubing, the end may be spun over to form its own washer so as to leave only one sealing surface at which leaks may occur (Fig. 4.39(*h*)). These joints can be heated repeatedly to 450° C without leaks occurring provided that the finish and freedom from radial scratches of the mating surfaces is adequate.

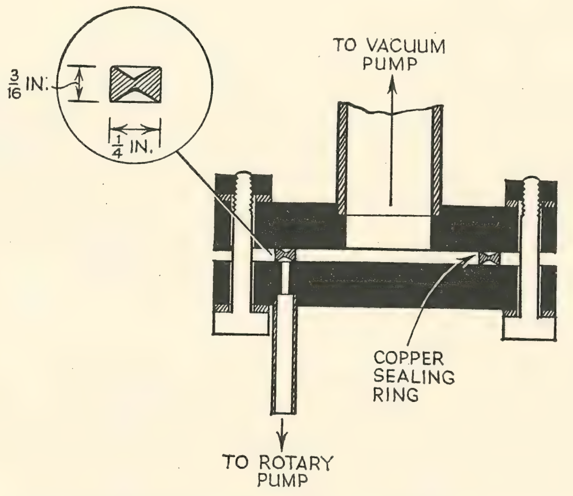


FIG. 4.40 A demountable metal gasket seal (*Heathcote and Read*)

Heathcote and Read (HR3) endeavoured to construct a demountable seal using stainless steel knife edges (an expansion match to copper) pressed into a copper gasket according to the designs of Pattee and van Heerden but report that they were only moderately successful at a diameter of $1\frac{1}{4}$ in. and unsuccessful at 4 in. if baked to 450° C, even though the copper gasket was carefully polished and hydrogen-stoved. This has also been the present writers' experience. Heathcote and Read therefore used standard copper steam jointing rings (manufactured by Hulburd Patents Ltd.) which were compressed between two steel flanges and the spaces between the contact edges evacuated by a rotary pump (Fig. 4.40). No leak was detectable after baking to 450° C, using a palladium leak detector (§ 9.8). Ground or well-turned surfaces on the steel flanges were used, also nickel-plated steel and 'K' Monel surfaces were successful, though chromium plating of the surfaces was unsatisfactory. The joints were dismantled and re-assembled several times; the light film of oxide which formed between the copper edges being removed with fine emery paper. Diameters of copper rings successfully used were 0·5 in. to 6 in., the compression of the ring being 0·030 to 0·040 in. Dimensions employed are given in Table 4.19.

TABLE 4.19

All dimensions in inches

O-ring		Flange		Bolts		Pitch
Outer dia	Inner dia	Dia	Thickness	No. of holes	Dia of holes	Circle dia
1	$\frac{1}{2}$	2	$\frac{3}{8}$	8	$\frac{17}{64}$	$1\frac{1}{2}$
$2\frac{1}{2}$	2	$3\frac{3}{4}$	$\frac{1}{2}$	8	$\frac{17}{64}$	3
$2\frac{3}{4}$	$2\frac{1}{4}$	4	$\frac{1}{2}$	12	$\frac{17}{64}$	$3\frac{1}{4}$
$3\frac{1}{4}$	$2\frac{3}{4}$	$4\frac{1}{2}$	$\frac{1}{2}$	12	$\frac{17}{64}$	$3\frac{3}{4}$
4	$3\frac{1}{2}$	$5\frac{1}{2}$	$\frac{1}{2}$	12	$\frac{17}{64}$	4
$6\frac{5}{8}$	$6\frac{1}{8}$	8	1	24	$\frac{17}{64}$	$7\frac{1}{4}$

Disappointment often accompanies the first use of metal ring gaskets especially if the joint is baked and repeatedly dismantled. Failure is usually due to inadequate surface finish of the mating surfaces, the presence of scratches, inadequate compression or non-uniformly applied compression. Repeated use of metal gaskets is unwise; in general, it is preferable to use a cheap, commercially available design (*e.g.* like that used by Heathcote and Reed) so that they can be discarded and replaced frequently. Conflicting reports appear frequently in the literature as to the virtues of one or other method of using these metal gaskets; these conflicting opinions are probably due to lack of attention to detail in construction rather than to extravagant claims of the originators.

Brymner and Steckelmacher (BS2) report excellent results with a new type of flat sheet gasket of soft copper, iron, stainless steel or nickel which is formed to a cone shape between the specially bevelled edges of the mating flange surfaces of mild or stainless steel (Fig. 4.41). This type of seal on flanges of 3 and 5 in. dia and on a $\frac{1}{2}$ in. vacuum union withstands repeated temperature cycling between −188° and +800° C. The seal depends on a surface-friction effect instead of compression only.

Indium (melting point 156° C) has been used in recent years for making vacuum seals. Reynolds (R12) describes three methods of application of the solid metal: (1) 0·050 in. dia indium wire in a groove between metal flanges to form a compression seal which is satisfactory if the surfaces are machined to a smooth finish; (2) the indium is soldered directly to the flange surfaces and then the flanges and a knife edge arrangement is employed for ensuring a high compression seal. All these methods are reputed to allow repeated re-sealing operations. Adam, Kaufman and Liley (AKL1) stress the advantages of indium as a gasket material in place of rubber or Neoprene where the presence of hydrocarbons in the vacuum system is undesirable and where external clamping is not possible so that aluminium, copper, lead, silver and tin cannot give a satisfactory seal. However, the low melting point of indium forbids its use in the solid form at baking temperatures above 120° C. They used indium wire of $\frac{1}{16}$ in. dia in the form of a ring retained in a trapezium shape channel (*cf.* Fig. 4.20(*c*)) cut in one of the metal surfaces to be joined. This channel was 0·059 in. wide and had maximum and minimum depths of 0·054 in. and 0·018 in. respectively, the tolerance being 0·001 in. This depth allowed a small ridge of indium to form between the sealing surfaces. After several days pumping, where the indium ring was in a channel in a brass flange with a polished Pyrex cover plate seated upon it, the thickness of the ridge was about 0·010 in. The indium ring was made by selecting a length of wire equal to the mean circumference of the groove minus a few millimetres, the ends were cut off square and butt-jointed in a small flame using Coraline soldering paste as a flux. The excess metal at the joint was pressed out in a jig and peeled off. Slight stretching to remove unevenness was then necessary to insert this ring in the channel. The minimum load necessary to ensure a seal was 5·9 kg wt per cm length of the wire so that it was possible to form vacuum seals on tubes of minimum diameter 23 cm by utilizing only the pressure of the atmosphere on a cover plate. Fig. 4.42 shows a standard vacuum union for tubing of $\frac{5}{8}$ in. dia in which an indium gasket was used instead of rubber. Vacuum seals using indium were also easily obtained with steel against steel, steel–porcelain and steel–aluminium alloy M27 (*British Aluminium Co., Ltd*). The surfaces used must be very clean and highly polished to ensure low leakage rates.

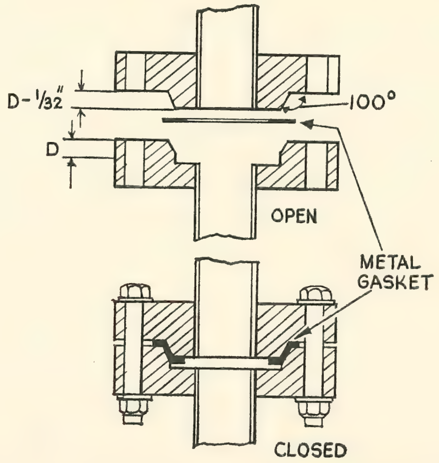


FIG. 4.41 A soft metal gasket between bevelled flanges (*Brymner and Steckelmacher*)

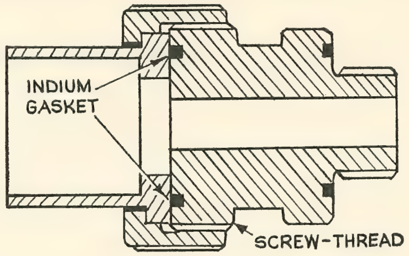


FIG. 4.42 A standard vacuum union with an indium gasket (*Adam, Kaufman and Liley*)

In that molten indium has a very low vapour pressure at elevated temperatures and a high boiling point (2100° C) it compares with tin but has considerably greater plasticity in the solid form. These features render this metal, like tin, useful for making demountable vacuum unions in which the indium is solid when the union is closed and is melted by passing current through a suitably placed Nichrome wire when it is required to break the joint. As this technique is most frequently applied in the design of special types of vacuum isolation valves, it is discussed in Chapter 5.

5

VACUUM PLUMBING II: ISOLATION VALVES AND GAS-METERING DEVICES

5.1. The Isolation of One Part of a Vacuum System from Another

In this context may be included (*a*) the sealing-off technique, *i.e.* the general case where a tube or container has been evacuated and processed and it is required to seal it off from the pump; (*b*) the use of stopcocks of both glass and metal, most of which employ a greased seal, though greaseless models have been developed; (*c*) cut-offs, *e.g.* mercury-filled types; (*d*) isolation valves utilizing a demountable seal, frequently of Neoprene. The ideal requirements in such procedures or of such devices may be listed as follows:

(*i*) Significant impedance to the flow of gas through the system should not be introduced, *i.e.* the throughput of the vacuum system should be impaired as little as possible.

(*ii*) Gases and vapours should not be evolved at the operating temperature.

(*iii*) The constructional materials used should be chemically inert to the gases and vapours handled. In particular, isolation valves made of metal should be rust-proof.

(*iv*) It should be possible to heat the isolation device to degas it.

(*v*) Rapid operation and, in some applications, good regulation of the gas flow, are desirable.

(*vi*) In most cases, freedom from gas leaks is necessary when the device is subjected to an external pressure of one atmosphere whilst a high vacuum exists internally.

(*vii*) Often, mechanical strength is desirable.

(*viii*) In the cases of stopcocks, cut-offs and isolation valves, the action should be positive and not adversely influenced by gas pressure differentials across the device.

These requirements will be considered where appropriate in the following sections.

5.2. The Sealing-off Technique

A frequently-encountered procedure in vacuum technology is the sealing-off of a glass vacuum tube from the pump after evacuation and processing. In the cases of small electron tubes and electric lamps, the practice is to use narrow glass pumping stems containing a pre-prepared constriction at which a seal-off is made by a blow-pipe flame. Degassing during seal-off is usually small as the tube is invariably baked-out during processing, but, if it is essential to minimize gas evolution, heating of the constriction in the flame just prior to seal-off is practised. These narrow pumping stems inevitably introduce high impedance to gas flow so restricting substantially the speed of evacuation. In the mass production of small vacuum tubes, this restriction is usually not serious, but it should be remembered that it makes the use of large pumps with high speeds a mere extravagance (§ 1.6). For sealing off small metal envelope thermionic tubes, cold pressure welding is often employed (§ 4.1).

In the pumping of large tubes like transmitting valves, mercury rectifiers and X-ray tubes, however, the restriction of the throughput of the vacuum system, due to the use of pre-constricted narrow pumping stems, is often a considerable disadvantage. In several cases, there is little alternative to arranging a sufficiently long-term pumping schedule to ensure adequate evacuation. There are, nevertheless, cases where undue gas evolution during processing demands that attention be paid to the conductance of the pumping stem.

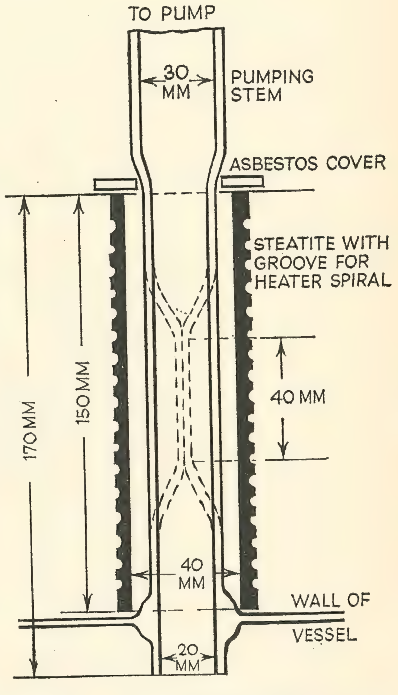


FIG. 5.1 Use of electrically-heated oven to seal off a tube of 20 mm internal diameter (*Adam*)

Adam (A6) describes a solution to this problem in connection with the pumping of large glass mercury rectifiers. He used a tubular-shaped electrically-heated oven to seal-off a Pyrex glass pumping stem of internal diameter 20 mm and conductance about 5 litre/sec (Fig. 5.1). The tubular oven (dimensions are given in Fig. 5.1) was made of steatite with a spiral groove cut in its outside walls in which was wound a Nichrome heater wire. Asbestos surrounded this heater to provide thermal lagging. To ensure an adequately uniform radial distribution of temperature, the separation between the glass tube and the inside oven wall must not be too small: about 8 mm suffices. The ends of the tubular oven were closed in with asbestos plates containing central holes. Experiment shows that the closing together of the glass pumping stem walls is not so uniform and symmetrical as when a constricted tube is correctly heated by a blow-pipe, but this does not matter. A correct time–temperature heating schedule should be arrived at by trial and always used to ensure success. Attempts are being made to seal off tubes of 30 mm inside diameter in this way and to ensure that, after seal-off, the pumping stem is as short as possible.

Roovers (R13) has patented a similar technique for sealing off the glass stems of television cathode-ray tubes where the thick wall of the stem may release gas during seal-off to the detriment of the tube vacuum. In order to effect closure of the stem, one half of the heater winding is connected to the electric supply to heat the section of the stem to 380° C for 6 min to degas it. The power supplied is then increased from 40 W to 150 W for about 25 sec, resulting in sealing off of the stem. The whole of the heater winding is then switched into the supply circuit and the power reduced to about 28 W. This permits annealing of the region around the seal-off over a period of 6 min.

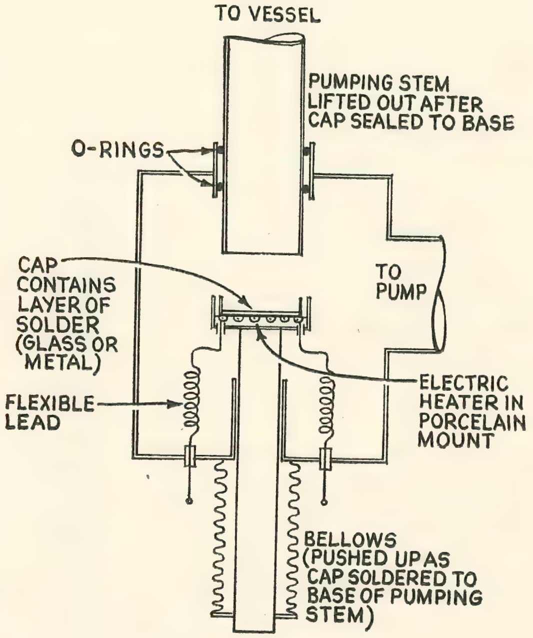

TO VESSEL
PUMPING STEM LIFTED OUT AFTER CAP SEALED TO BASE
O-RINGS
CAP CONTAINS LAYER OF SOLDER (GLASS OR METAL)
TO PUMP
FLEXIBLE LEAD
ELECTRIC HEATER IN PORCELAIN MOUNT
BELLOWS (PUSHED UP AS CAP SOLDERED TO BASE OF PUMPING STEM)

FIG. 5.2 Suggested method for sealing-off wide bore pumping stems

There exists the possibility of using in routine production the technique of making a closure to a wide pumping stem tube by inserting a glass disc (for a glass tube) or a metal disc (for a metal tube) into place and then making a vacuum-tight seal either with a glass solder or with a metallic solder like tin or indium, both of which have low melting points and very low vapour pressures at elevated temperatures. A suggested arrangement for this purpose is shown in Fig. 5.2. Extended trials on such a procedure might well be worth while.

Various methods have been devised for sealing off a container within an evacuated tank. Figure 5.3 illustrates a procedure based on that described by Holland-Merten (H5) for filling with solder the small opening in the lid of a can within a vacuum tank; Fig. 5.4 shows the principle of an ingenious method devised by Dr. F. C. Weil (*private communication*) in which an inflatable seal is used to apply closing pressure to the lids on a number of glass jars within an evacuated tank.

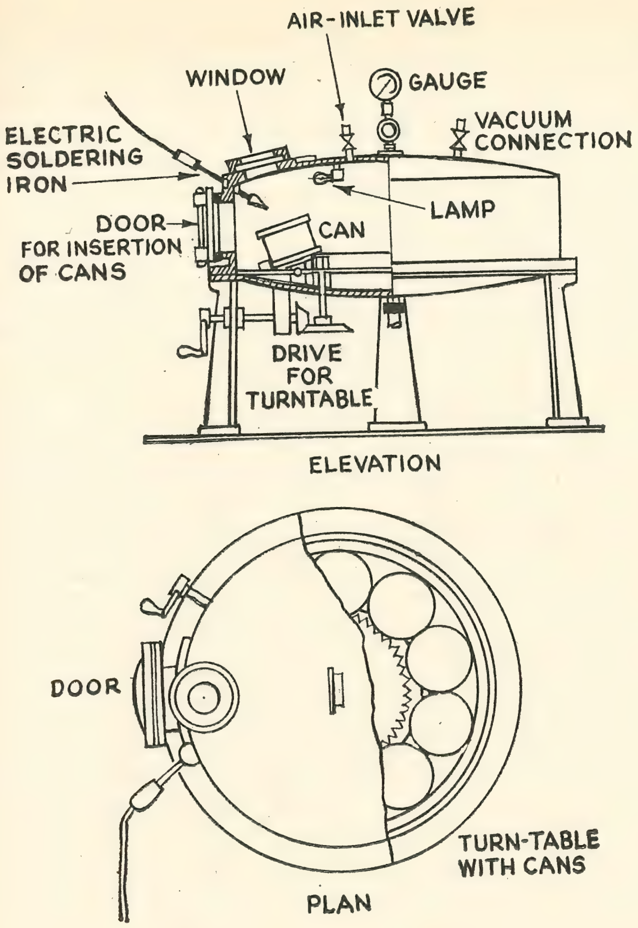

AIR-INLET VALVE
WINDOW
GAUGE
VACUUM CONNECTION
ELECTRIC SOLDERING IRON
LAMP
DOOR
FOR INSERTION OF CANS
CAN
DRIVE FOR TURNTABLE
ELEVATION
DOOR
TURN-TABLE WITH CANS
PLAN

FIG. 5.3 Arrangement for sealing metal containers by soldering under vacuum

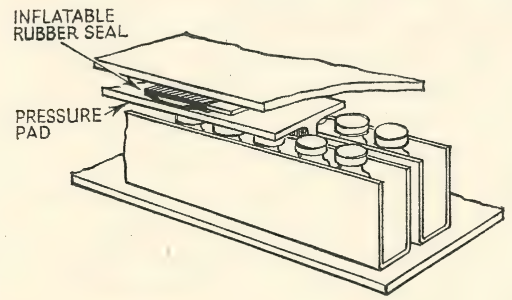

INFLATABLE RUBBER SEAL
PRESSURE PAD

FIG. 5.4 Use of an inflatable seal to apply pressure to jar-lids under vacuum

5.3. Stopcocks

The use of glass stopcocks is so familiar as to demand little further description. The basic designs used in vacuum practice are illustrated in Fig. 5.5. These employ mating ground glass conical joints which are lubricated and sealed with Apiezon or silicone greases. Metal stopcocks of similar patterns are used, but they have been largely replaced by the advent of the widely-used isolation valves employing rubber seals.

Glass stopcocks, though invaluable and widely used on glass vacuum systems in that they are cheap in small sizes, give air-leak free seals, are readily operated and installed, and can be used to regulate gas flow to some extent, suffer from the following disadvantages in relation to the ideal requirements outlined in § 5.1.

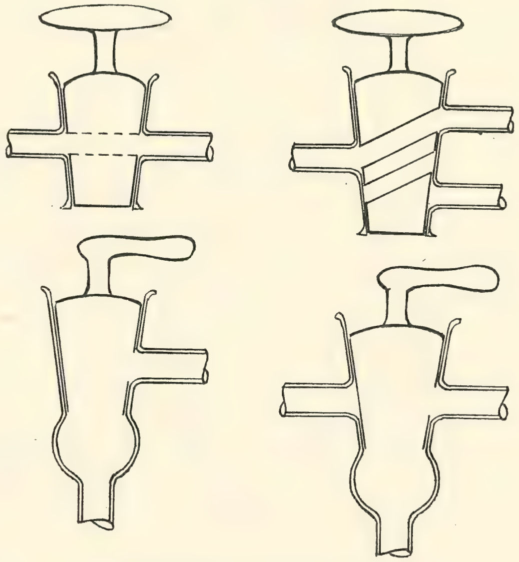


FIG. 5.5 Glass stopcocks

(*i*) It is virtually impossible to design glass stopcocks with an effective bore of more than 50 mm and, moreover, such large taps would be expensive and difficult to turn. This means that the maximum conductance to gas is limited; indeed, it is not practicable to use a glass stopcock where an overall pumping speed of more than 20 litre per sec is required.

(*ii*) The vapour pressure of vacuum grease is about 10^{-6} torr at room temperature. More important, in many cases the grease tends to evolve occluded gas, especially when the stopcock is turned.

(*iii*) The grease is attacked by many organic vapours.

(*iv*) It is not possible to heat the tap to above about 30° C without causing the grease to flow undesirably.

(*v*) Glass types often seize up after prolonged use unless they are re-greased regularly. They are also fragile.

Metal stopcocks have been used to some extent in vacuum technology but chiefly in small sizes and where pressures less than 10^{-2} torr are not required. It is difficult to grind metal stopcocks so satisfactorily that, on prolonged use, they maintain a really adequate seal.

Greaseless stopcocks. To provide the convenience and simplicity of the glass stopcock but without the necessity for the use of grease has been the object of several designs. Springham and Company market the model illustrated by Fig. 5.6, in which a plug of silicone rubber is screwed down on to the end of a capillary tube to provide a seal; this has been found useful by the authors as a means of regulating the gas flow into a vacuum system from a container of gas at about 1 torr pressure. It is available in bore diameters of 1 to 4 mm. Stanier and Beynon (SB1) use a glass tap with colloidal graphite lubrication, where mercury is used for sealing. Other designs, *e.g.* the useful arrangement of non-greased fitting glass hemispheres, are really isolation valves and will therefore be described later. The plug valve (§ 5.13) is also classifiable as a stopcock.

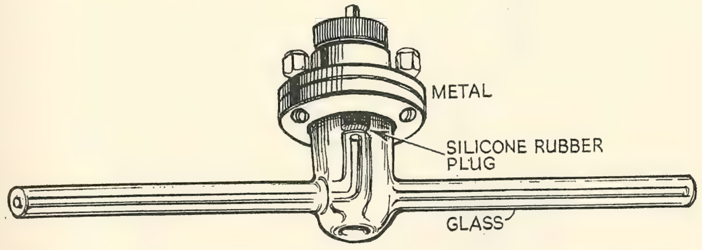


FIG. 5.6 A greaseless glass stopcock (*Springham and Company*)

5.4. Cut-offs

Four types of mercury cut-off are shown in the self-explanatory diagrams in Fig. 5.7. That of Fig. 5.7(*c*) is preferred as it can be simply operated magnetically and does not require the use of a mercury-filled reservoir of which the height can be altered. Haul and Swart (HS2) describe a magnetic mercury cut-off of small volume, able to deal with large pressure differences without risk of flooding the system with mercury, and also to maintain a vacuum of 10^{-6} torr or less, in which, to close the cut-off, the stainless steel ring S (Fig. 5.7(*d*)) is first pulled down into the reservoir R by means of the magnet M. The mercury is then frozen by solid carbon dioxide in a surrounding Dewar flask. To open the cut-off the magnets are raised and clamped in position by the screw T.

5.5. Isolation Valves: Classification of Types

In an attempt to classify the many kinds of isolation valve that have been introduced, six main types are considered (*see also Glossary of Terms Used in Vacuum Technology*, Committee on Vacuum Standards, American Vacuum Society, Inc.).

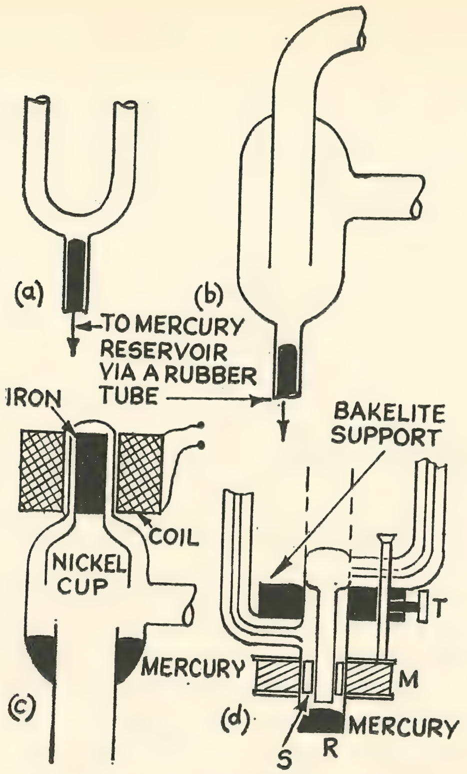


FIG. 5.7 Mercury cut-offs

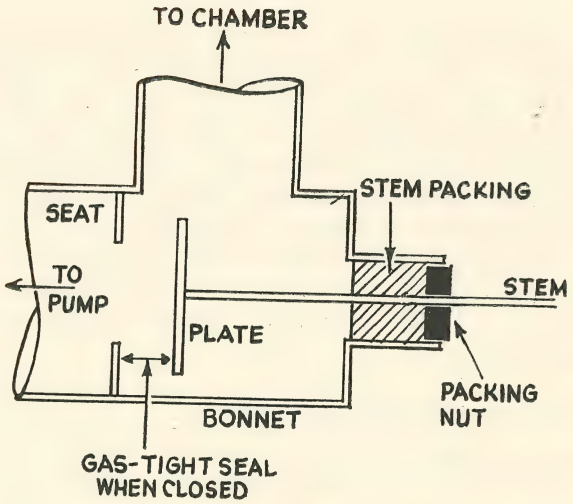


FIG. 5.8 Main features of packed isolation valves

(*a*) The most common type is the **packed valve,** in which packing material is inserted between the valve stem and the valve bonnet to prevent leakage (Fig. 5.8). This seal is generally of Neoprene (preferred to rubber) and in the form of a Wilson seal (§ 4.24), a sleeve or washer, or one or more O-rings (§ 4.17), though oil-filled seals are also used. On closing the valve, a vacuum-tight seal must also be effected where the valve plate meets the valve seat. This is most frequently arranged by a Neoprene O-ring.

(*b*) **The packless valve** in which the seal between the stem and bonnet of the valve is positive. Examples are the **bellow-sealed valves** in which the use of flexible metal bellows ensures vacuum-tightness at this seal, and valves in which a corrugated, flexible metal diaphragm is used; **ultra-high vacuum valves** of the Alpert pattern are of the latter pattern. In general, it is not possible to transmit as large a degree of motion to the valve plate via a bellows as it is via a packed stem; if a flexible diaphragm is used, then this motion is severely restricted. Certain types of **magnetically-operated glass valves** may also be classified as packless valves.

(*c*) **The diaphragm valve** in which a flexible diaphragm is used to effect the main isolation seal.

(*d*) **The gate valve** in which a vane or disc is slid or rotated into and also sealed in the cross-section (usually circular) of the body of the valve between its inlet and outlet openings.

(*e*) **The plug valve** which contains a plug that is moved or rotated inside the valve body so that a hole in the plug registers with corresponding holes in the body.

(*f*) **The ball valve** in which a ball is rotated inside the valve body so that a bore hole through the ball can be aligned with the inlet and outlet openings of the valve. This is not a popular type in vacuum technology and will not be considered further.

Though most isolation valves can be placed in one of these categories, there are some designs which could be classified differently, *e.g.* models which could be considered as either packed valves or gate valves.

5.6. Packed Isolation Valves with Neoprene Sealing Between the Plate and the Seat

In general, oil-resisting Neoprene is preferred to natural rubber. A wide variety of valves of these types has been described in the literature and is used in practice. If suitably designed they can have the outstanding advantages of high conductance to gas flow, rapid operation in some cases and great mechanical strength. The chief disadvantages are that they cannot be degassed adequately by baking and that gases and vapours are evolved by the Neoprene. This means that these valves are essentially used in kinetic and not in static vacuum systems.

Many workers have utilized existing valves as used in general engineering, liquid, gas or steam practice and modified them for vacuum work. In general, these modifications are to dismantle the valve, clean it, machine certain surfaces to a higher precision and then introduce Neoprene discs, gaskets or O-rings to ensure a vacuum-tight seal between the valve plate and seat when closed. It is also usually necessary to remove the packing between the valve stem and the bonnet and replace it by a rubber gland, Wilson seal, or an O-ring. Neoprene gaskets are usually sparingly coated with vacuum grease or oil and, in some cases, the internal metallic surfaces of the valve are electroplated to ensure resistance to corrosion. Valves with internal-bore diameters from $\frac{1}{2}$ to 2 in. can be successfully made in this way and are used extensively in metal vacuum systems where pressures in the region of the valve are not less than 10^{-3} torr, *i.e.* in the backing line, though, in some cases, pressures as low as 10^{-5} torr can be used.

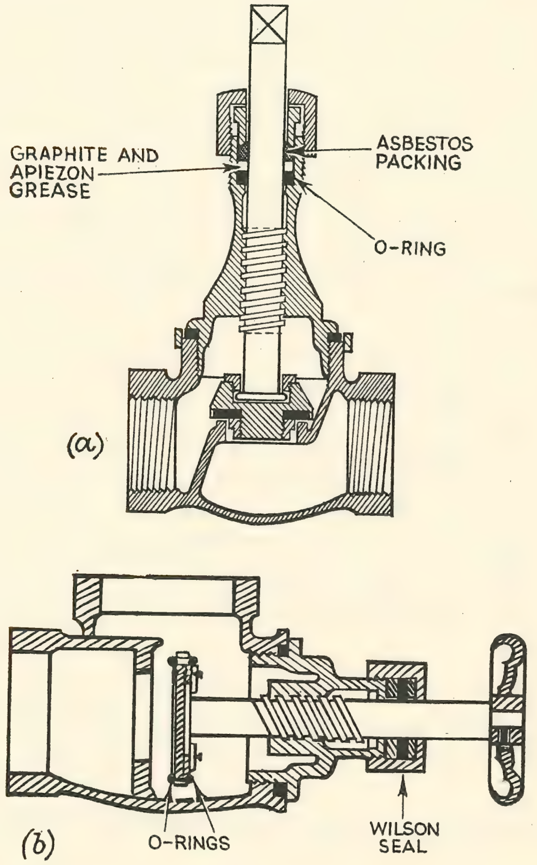


FIG. 5.9 Packed vacuum isolation valves derived from gas and steam valves

Figure 5.9(*a*) shows a design due to Moore (M9) who used a Neoprene O-ring for packing; Fig. 5.9(*b*) illustrates a modification by Cowie and Green (CG1) of a Stockham 2 in.-angle steam valve which utilizes a Wilson seal for stem-packing.

The second method adopted has been to design isolation valves specifically for vacuum work. Usually, this applies to larger valves with bore diameters in the range from 2 to 30 in. and, particularly, for operation in the fine-side region of a vacuum system where pressures down to 10^{-6} torr may be encountered.

D'Eustachio (D9) has designed a valve in which the square plate is guided on four rods and is operated by a cam (Fig. 5.10(*a*)). Helical springs on the rods push against the plate to ensure that it follows the cam. The packing gland consists of thoroughly-cleaned steel wool in a silicone oil-bath between cleaned, dried asbestos pads. The rubber gasket plate-to-seat seal is in a suitably-shaped groove in the valve seat. This worker recommends that rubber or Neoprene gaskets be degassed before use by heating them *in vacuo* at 70–80° C. A number of these valves with aperture diameters ranging from $\frac{1}{2}$ to 2 in. were constructed.

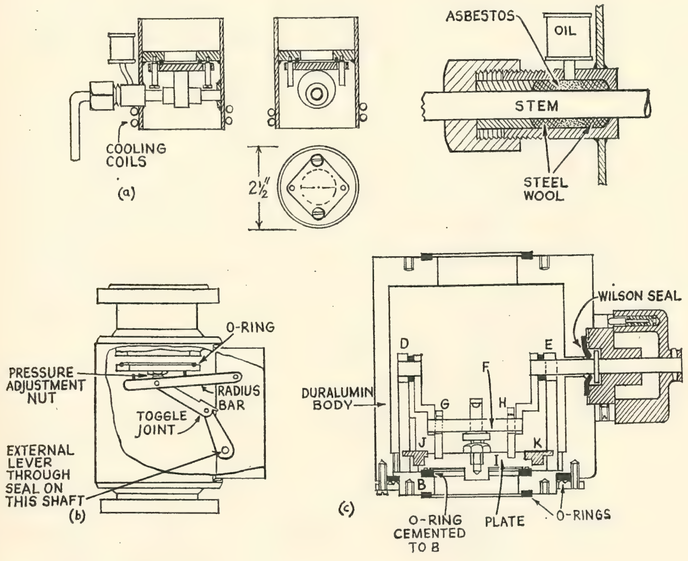


FIG. 5.10

(*a*) Cam-operated isolation valve with oil-filled gland (*D'Eustachio*)
(*b*) Straight-through valve (*Jennings*)
(*c*) A low impedance valve (*Garrod*)

Jennings (J5) describes a 6 in. dia valve (Fig. 5.10(*b*)) which has a large straight-through passage when open. This valve can be closed rapidly in case of breakdown—a likely possibility in particle accelerators like the Van de Graaff accelerator for which the valve was designed. The plate-to-seat seal is a Neoprene O-ring within a groove in the plate. The operation of the plate is via a lever structure comprising three bars—one is a radius bar to hold the plate centrally over the seat when closed, and the other two form a toggle joint; a Wilson seal is used for packing.

A valve due to Garrod (G8) with a $1\frac{1}{2}$ in. aperture (Fig. 5.10(*c*)) has a duralumin body for lightness. A rectangular section O-ring is cemented on the duralumin valve seat and the plate has two circular ridges which embed in this gasket when the valve is closed. A Wilson seal is used for the stem packing gland. Two vertical pillars *D* and *E* support a crankshaft *F* of which the horizontal shaft passes through two slotted vertical members *G* and *H* attached to the plate *I*. Two pins *J* and *K* on this plate slide in vertical slots in *D* and *E* respectively. The pin *J* is shaped like a small bell-crank and, during the first 90° of rotation of the crankshaft *F* from the closed position, the flat side of the pin *J* bears against a fence attached to the pillar *D* so that the plate *I* must rise vertically without rotation. On rotating the crankshaft further, the pin *J* is disengaged from the fence and the plate *I* swings into a vertical position.

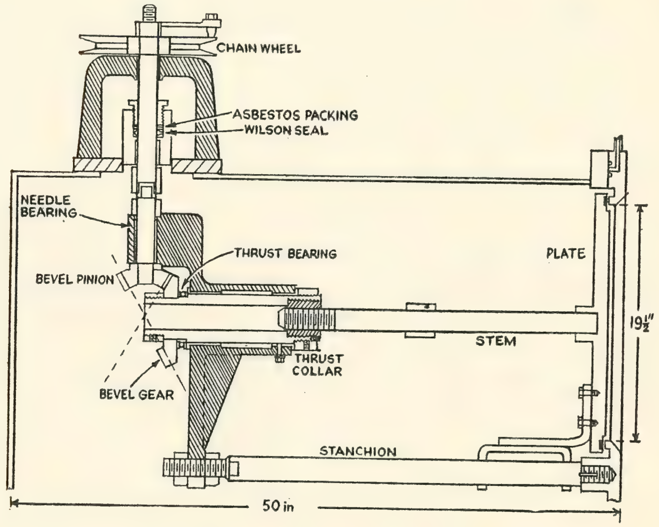

CHAIN WHEEL
ASBESTOS PACKING
WILSON SEAL
NEEDLE BEARING
THRUST BEARING
PLATE
BEVEL PINION
STEM
THRUST COLLAR
BEVEL GEAR
$19\frac{1}{2}$"
STANCHION
50 in

FIG. 5.11 Chapman 20-in. disc valve (*based on a diagram given by Guthrie and Wakerling*)

Guthrie and Wakerling (GW1) give detailed diagrams of Chapman isolation valves (Chapman Valve Manufacturing Company) including a 6-in. (4-in. aperture) angle valve, a 20-in. disc valve (the stem drive being via a chain wheel) and a 30-in. disc valve (motor-driven stem). The essential features of the 20-in. valve are shown in Fig. 5.11.

Further designs of isolation valve available commercially are illustrated in Fig. 5.12. A straight-through design used by Edwards High Vacuum Ltd. on their (2 to 16 in.) oil diffusion pumps is illustrated in principle by Fig. 5.12(*a*). This valve, like similar designs, acts when open, or partially open, as a fairly efficient baffle against back-streaming (§ 2.10). Two designs amongst others made by Leybold are a right-angle valve (Fig. 5.12) and a plate valve of particularly low height (Fig. 5.12(*c*)). The flap-valve of the design shown in Fig. 5.12(*d*) is available in four different sizes (max inlet aperture diameter $2\frac{7}{8}$ in.) from the Associated Electrical Industries (Manchester) Ltd.

These four examples are only meant to be representative of commercial designs; a range of sizes of valve for both medium and high vacuum work are available from all the main vacuum equipment suppliers (*see* Appendix D), though some prefer packless designs (§ 5.8).

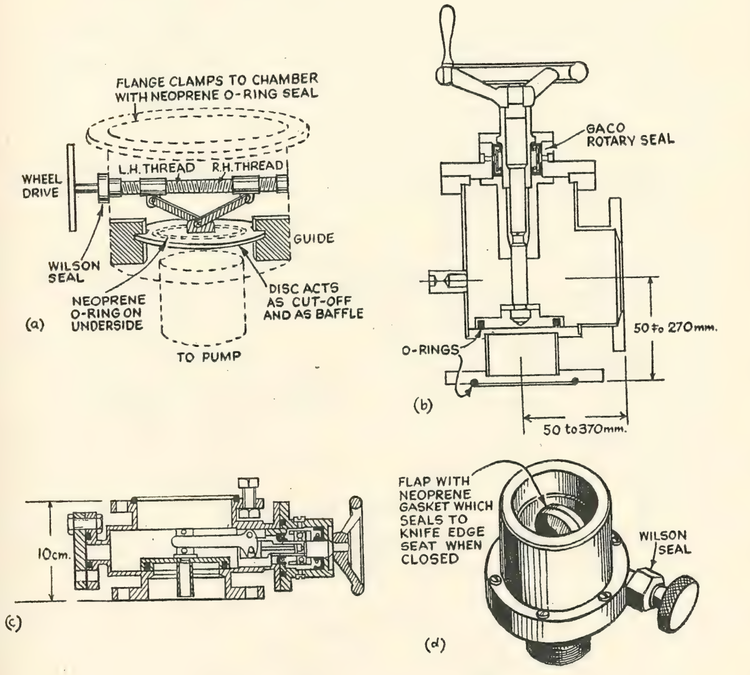

FLANGE CLAMPS TO CHAMBER WITH NEOPRENE O-RING SEAL
L.H. THREAD
R.H. THREAD
WHEEL DRIVE
GUIDE
WILSON SEAL
NEOPRENE O-RING ON UNDERSIDE
DISC ACTS AS CUT-OFF AND AS BAFFLE
TO PUMP
(a)
GACO ROTARY SEAL
O-RINGS
50 to 270mm.
50 to 370mm.
(b)
10cm.
(c)
FLAP WITH NEOPRENE GASKET WHICH SEALS TO KNIFE EDGE SEAT WHEN CLOSED
WILSON SEAL
(d)

FIG. 5.12

(*a*) A water-cooled baffle valve (*Edwards High Vacuum Ltd.*)
(*b*) A right-angle valve (*Leybold*)
(*c*) Plate valve of low height (*Leybold*)
(*d*) A flap valve (*A.E.I.* (*Manchester*) *Ltd.*)

5.7. Other Designs of Packed Isolation Valves

Lang (L8) describes a valve made from drawn brass with a copper plate to soft brass seat seal without rubber for use on a vacuum spectrograph (Fig. 5.13(*a*)). The valve seat consists simply of a raised rim of soft brass about $\frac{1}{8}$ in. wide and $\frac{1}{16}$ in. high, whilst the valve plate is a piece of soft brass with a copper plate inset in its lower face; this copper fits over the seat when the valve is closed. The surfaces involved are not ground but finished smooth on the lathe.

Green (G9) uses a steel cone against a soft copper seat to make the seal in a small valve (Fig. 5.13(*b*)). As an O-ring is essential to ensure vacuum-tight packing of the stem, this valve cannot be baked to degas it; however, when closed, rubber is not exposed to the vacuum.

Simple greaseless valves suitable for gas pressures above about 10^{-2} torr and based on polyethylene or polyvinylchloride tubing are described by Raats, Harley and Pretorius (RHP1). Examples are shown in Fig. 5.14. Under pressure, polyethylene 'wets' glass so that plugs of this material should fit tightly to ensure a gas-tight seal. In the valve of Fig. 5.14(*a*) a seal is effected by compressing a short length of elastic, heavy-walled polyvinylchloride tubing (or rubber could be used) against the body of the valve which is made from glass tubing. The annular gap between the tubing and the walls should not exceed 1 mm when the valve is open. A gas-tight fit between the threads of the metal stem and the polyethylene packing of the valves shown in Fig. 5.14 ((*a*) and (*b*)) is effected by drilling and threading the hole in the packing to be slightly smaller than the stem; the stem is heated to about 100° C and worked into the screw threads of the packing.

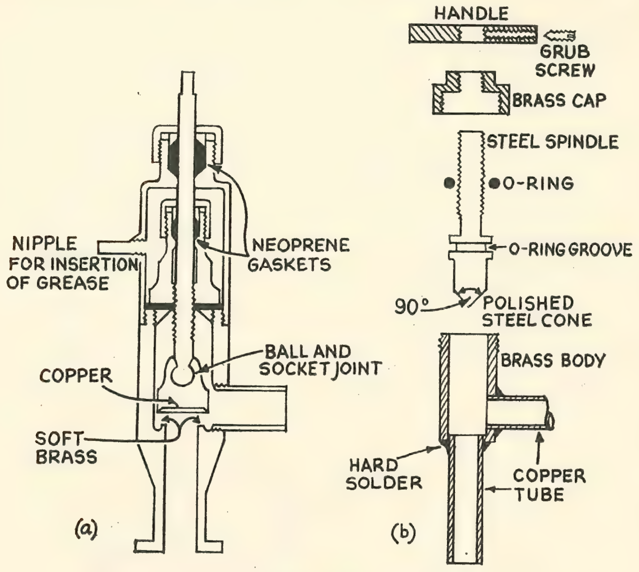


FIG. 5.13

(*a*) Packed valve with metal-to-metal seal (*Lang*)
(*b*) Metal-to-metal vacuum valve (*Green*)

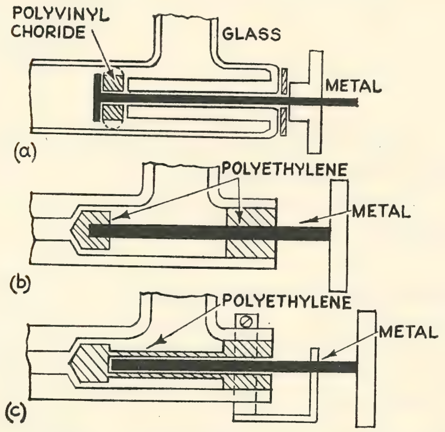


FIG. 5.14 Simple valves in which sealing is effected by polyethylene or polyvinylchloride

5.8. Packless, Bellows-sealed Valves

Several designs are available in which a positive metal-bellows seal between the connection to the valve plate and the valve bonnet is preferred to a packed gland. Such valves give greater freedom from possible leakage than the packed types, but the motion that can be applied to the valve plate is limited; also, they are more difficult to manufacture and repair, and the bellows are liable to crack with repeated use, though this last disadvantage is a slight one in a well-designed valve. If sylphon or tombac bellows are used, they must not be exposed to mercury vapour.

Rose (R14) has modified a design due to Dumond (D10) and gives details of a bellows-sealed valve based on a Jenkins 1-in. Y steam-valve made of bronze (Fig. 5.15(*a*)) and in which the plate-to-seat seal is by means of a Neoprene washer. Though a sliding seal is necessary where the valve stem enters the bonnet, this seal does not have to be gas-tight because it is separated from the vacuum system by the soldered-in bellows. Krohn (K9) describes a valve using a Neoprene gasket seal between the plate and seat which has been made in diameters of 1 in., 2 in. and 6 in. To avoid undue length of travel of the bellows used for stem-to-bonnet sealing, and so prolong their operational life, and yet permit adequate motion of the valve plate, a rack-and-pinion drive mechanism is used on the vacuum side, (Fig. 5.15(*b*)). A minor feature of this valve worth noting is that all close-fitting parts within the valve such as screws, etc., have small pump-out grooves to permit rapid evacuation of air pockets. Grivet and Blattman (GB1) give details of a design of valve in which the bellows extension is limited to 15% but where a much larger translatory motion may be imparted to the valve plate via a 'lazy-tong' linkage.

Lockenvitz, Hughes, Lipson and Olewin (LHLO1) have designed a bellows-sealed valve for use on a mass spectrograph (Fig. 5.15(*c*)). A feature of this valve is the use of two valve plates each of which bed on to Neoprene gaskets, so that, in the open position of the valve, the air inlet, the exhaust hole to an auxiliary pump, and the sylphon bellows are sealed from the main vacuum system.

Two designs of bellows-sealed valves are shown in Fig. 5.16. A National Research Corporation (also Vacuum Industrial Applications Ltd.) 6-in. model (Fig. 5.16(*a*)) employs Neoprene plate-to-seat sealing. Packless valves of sizes 1 in., 3 in., 10 in. and 16 in. are also made by this firm. Kinney valves (Kinney Manufacturing Company, and also General Engineering Co., Ltd.) also supply bellows-sealed valves in the following sizes: 1 in., 1½ in., 2 in. and 3 in. A smaller design of bellows-sealed valve is illustrated in Fig. 5.16(*b*).

Bakeable bellows-sealed valves. A most useful feature of the bellows-sealed valve as compared with the packed valve is that designs are possible in which

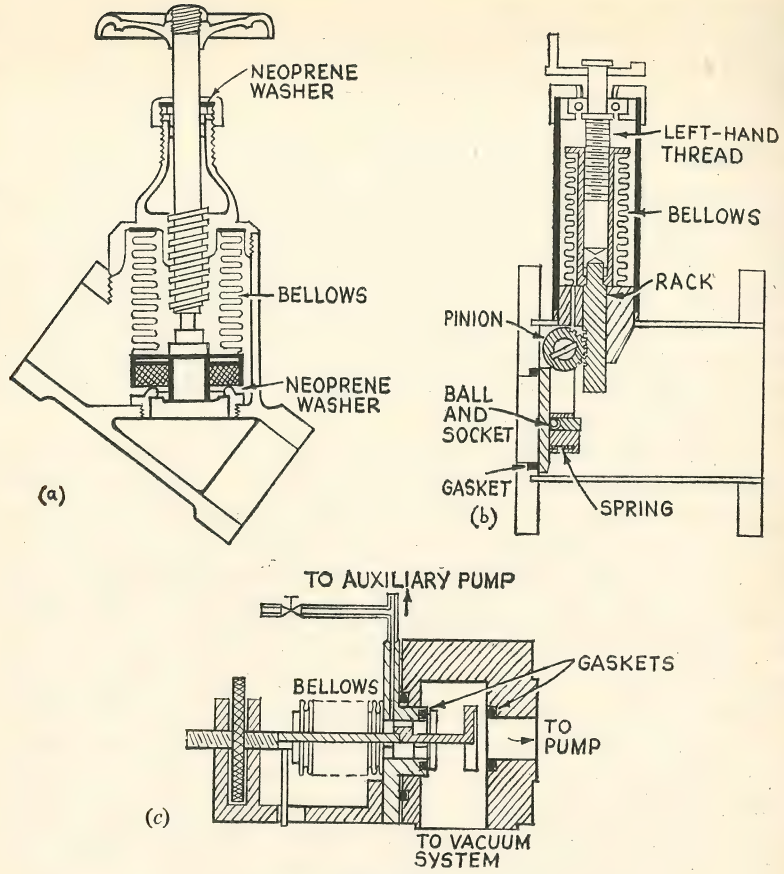

NEOPRENE WASHER
BELLOWS
NEOPRENE WASHER
(a)
LEFT-HAND THREAD
BELLOWS
RACK
PINION
BALL AND SOCKET
GASKET
SPRING
(b)
TO AUXILIARY PUMP
GASKETS
BELLOWS
TO PUMP
(c)
TO VACUUM SYSTEM

FIG. 5.15

(*a*) Bellows-sealed valve (*Rose*)
(*b*) Bellows-sealed valve with rack-and-pinion drive (*Krohn*)
(*c*) Bellows-sealed valve for mass spectrograph (*Lockenvitz et al.*)

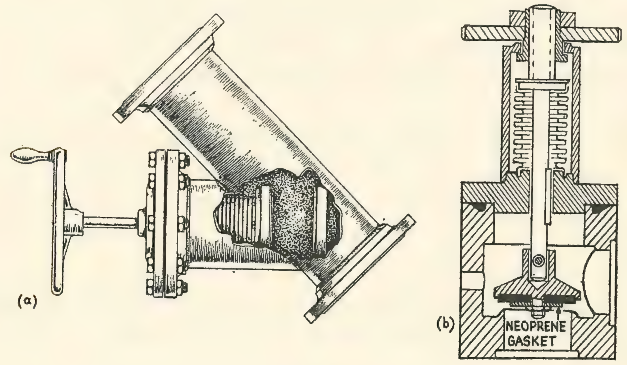

(a)
(b)
NEOPRENE GASKET

FIG. 5.16

(*a*) Bellows-sealed 6-in. valve (*National Research Corporation*)
(*b*) Bellows-sealed valve

---

degassing by heating may be undertaken. Neoprene sealing of the plate-to-seat is then not admissible but designs in which a metal-to-metal and also a glass-to-silver chloride seal is used have been published. A further possibility is to employ tin for making the plate-to-seat seal; the tin is then melted by passing current through a suitably placed heater when it is required to break the seal. The possibilities of bakeable valves of these types have not been fully exploited; recent developments have been concerned with valves using corrugated diaphragm sealing between the stem and bonnet rather than metal bellows (§ 5.9).

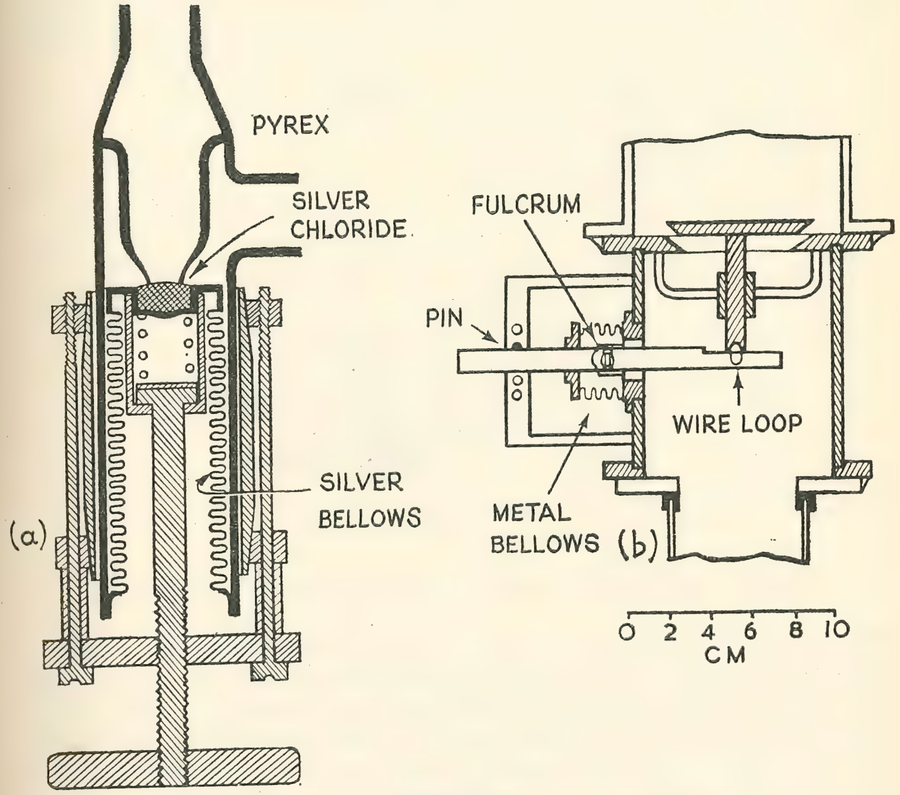

PYREX
SILVER CHLORIDE
SILVER BELLOWS
(a)
FULCRUM
PIN
WIRE LOOP
METAL BELLOWS
(b)
0 2 4 6 8 10
CM

FIG. 5.17

(*a*) A greaseless and chemically inert valve (*Rampsberger*)
(*b*) An all-metal bellows-sealed valve (*Estermann and Foner*)

Bellows-sealed valves, without Neoprene plate-to-seat sealing, which have been described in the literature have been intended chiefly for vacuum systems in which it is required to exclude rubber or grease rather than to enable a degassing bake-out to be undertaken. Rampsberger (R15) has designed a valve in which a seal is effected between fused silver chloride and the orifice at the mouth of a shaped Pyrex glass tube when the valve is closed (Fig. 5.17(*a*)). Silver bellows are fused to a glass tube at their lower end, whilst, at their upper end, a cup-shaped depression contains the silver chloride. The valve is operated by the screw attachment shown, the working of which is obvious from the diagram. This valve does not appear to have been used to any notable extent, probably because it is difficult to construct. Estermann and Foner (EF1) describe a valve for sealing off a port diameter of 3½ in. The valve plate is a circular brass disc with a ground conical edge which fits, when the valve is closed, into the correspondingly ground edges of a circular aperture in a brass plate as the valve seat. The valve plate is movable relative to the valve seat by a lever passing through tombac or sylphon bellows, which can be flexed (Fig. 5.17(*b*)). This valve has a conductance of more than 100 litre per sec when open and of a few cc per sec when closed. This imperfect sealing when closed can be tolerated in several applications. This valve would not be satisfactorily bakeable because it employs zinc-bearing alloys in its construction, and zinc volatilizes readily on heating *in vacuo*. However, a bakeable valve of this type constructed of Monel metal or stainless steel might well prove useful in the design of all-metal vacuum systems.

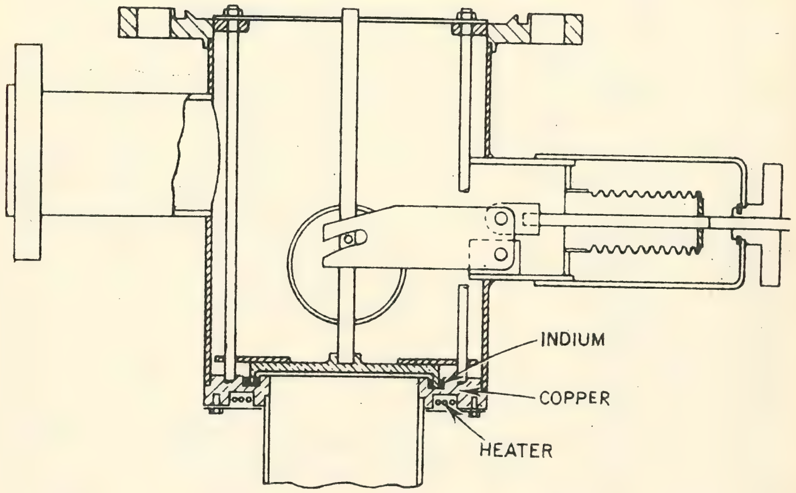
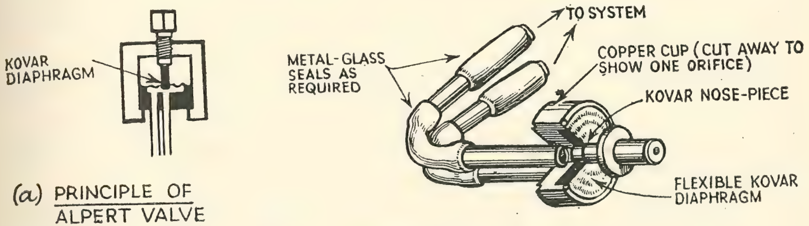


FIG. 5.18 Metal bellows-sealed valve with an indium seal (*Reynolds*)

An all-metal bellows-sealed valve using an indium seat is described by Reynolds (R12). Again, this valve was not degassed by baking but was designed for use in a mass spectrometer employing electron multiplier detection (§ 3.12) which becomes sensitive to the presence of hydrocarbons if any organic material is used in the vacuum system. The valve is made from a copper block (Fig. 5.18). A groove milled in the top (inside the vacuum) surface of the copper valve seat is filled with indium, whereas the groove in the lower (in air) surface contains a spiral Nichrome heater operated from the a.c. mains supply. Two minutes are required to melt the indium (melting point: 155° C) so that the valve plate can be raised. A valve of this type which would be heated to 200° C would need to employ tin (melting point: 232° C) in place of indium. Both indium and tin have very low vapour pressures at elevated temperatures; for tin, the vapour pressure is 10^{-5} torr at 823° C.

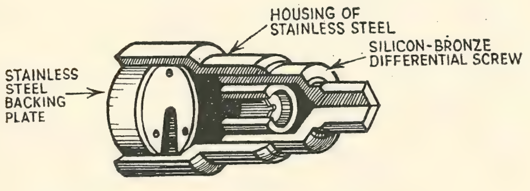
5.9. Packless, Diaphragm-sealed Valves; Ultra-high Vacuum Valves

The increasing interest of recent years in ultra-high vacuum (pressures below 10^{-7} torr) has led to the design of ultra-high vacuum valves which are made of metal and which can be thoroughly degassed by baking at about 450° C. The designs so far employed have flexible metal diaphragm sealing between the valve 'stem' and the bonnet and a plate-to-seat seal in the form of a hard metal nose forced hard (when the valve is closed) against a softer metal seat. The use of metal bellows sealing is a likely future development in ultra-high vacuum valves of large conductance when open.

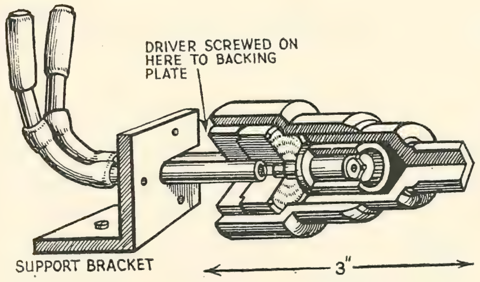

KOVAR DIAPHRAGM
METAL-GLASS SEALS AS REQUIRED
TO SYSTEM
COPPER CUP (CUT AWAY TO SHOW ONE ORIFICE)
KOVAR NOSE-PIECE
FLEXIBLE KOVAR DIAPHRAGM

(*a*) PRINCIPLE OF ALPERT VALVE

(*b*) THE VALVE ASSEMBLY


HOUSING OF STAINLESS STEEL
SILICON-BRONZE DIFFERENTIAL SCREW
STAINLESS STEEL BACKING PLATE

(*c*) THE DRIVER MECHANISM



(*d*) THE COMPLETE VALVE

FIG. 5.19 Ultra-high vacuum valve (*Alpert*)

The pioneer design is due to Alpert (A7). In principle, it is very simple: a solid copper cup contains two 0·25-in. dia holes. Kovar tubes are soldered into each of these apertures and these tubes are connected, usually via glass tube to Kovar seals (§ 4.7) to the vacuum line in question. A solid Kovar nose-piece is then forced into one of these holes to isolate one connecting tube from the other (Fig. 5.19(*a*)). This nose-piece forms in effect, both the 'stem' and the 'plate' of the valve and it is sealed to the periphery of the copper cup by a flexible Kovar diaphragm. The copper cup is 1·75 in. in diameter and the Kovar diaphragm, which permits a to-and-fro movement at its centre of about 0·1 in., is soldered to the copper cup at its periphery and to the Kovar nose-piece at a central hole. The nose of the Kovar member has a highly polished, 45° conical surface which forms its own seat in the edge of the central hole in the copper cup when it is closed for the first time. Oxygen-free, high conductivity (O.F.H.C.) copper must be used and all the joints are brazed using eutectic silver–copper solder (§ 4.2) without flux in a hydrogen stove (§ 4.3). The valve assembly produced is then free of surface oxides and extremely clean (Fig. 5.19(*b*)).

Movement in and out of the Kovar nose-piece to close and open the valve is by means of a 'driver mechanism' which is removed during baking of the valve, the valve being meanwhile retained in its open position by a U-shaped stainless-steel strap called a 'bake-out clamp'.

This driver mechanism (Fig. 5.19(*c*)) consists of a differential screw with a large mechanical advantage which moves the Kovar nose-piece about 0·01 in. per revolution and provides a total travel of 0·1 in. It consists of four parts: (*a*) an outside screw and housing of stainless steel; (*b*) a silicon–bronze differential screw with a thread pitch of 20 per in. outside and 26 per in. inside; (*c*) a stainless-steel driver screw which is fitted to the valve nose-piece; (*d*) a stainless-steel backing plate which is securely and rigidly bolted to a permanent bracket on the bench and designed to withstand the large thrust exerted on the copper cup when the valve is closed. The differential screw has a square head of 0·5 in. side which is turned by a suitable key, spanner or wrench. This enables forces of 5 to 10 tons to be exerted on the Kovar nose-piece so that it is compressed hard against the copper seat when the valve is closed. Loops in the glass tubing to the valve ensure against fracture when the valve is operated.

The conductance of this valve when closed is reputed to be 10^{-11} litre per sec, *i.e.* it is virtually a perfect vacuum seal for most practical purposes. In use, slight oxidation and wear of the smooth nose-piece and copper seat lead to deterioration. Alpert reports an increase of the conductance of his valves to 10^{-10} litre per sec after a year's use; other workers have observed increases to 10^{-6} litre per sec after prolonged use. Though still a negligible value for most applications, this undue increase is probably due to baking the valve when the internal gas pressure is too high, *i.e.* above 10^{-6} torr, so producing slight oxidation.

Ultra-high vacuum valves of this type are supplied in Britain by Mullard Ltd. (Materials Division). They are used in the production of gas pressures down to 10^{-10} torr (§ 8.3) and also as most valuable gas-metering devices (§ 5.17). They are conveniently supplied with an attached electric heater for bake-out purposes.

Yarwood (Y4) and also Baker and Yarwood (BY1) describe an Alpert valve (sometimes known as an 'Alpert tap') in which the soldering was undertaken in an evacuated silica tube, the necessary heat being supplied by a suitably disposed induction heater coil. The use of an induction coil enabled

the heating to be substantially localized in the region of the joint to be made. Thus, the glass tubes fused to the Kovar tubes were already in position but suffered no harm during soldering. A hydrogen-filled stove is, however, preferred to a vacuum stove as the product is cleaner and more free of surface oxidation.

Brown and Coyle (BC1) have designed an ultra-high vacuum valve which is a development from the Alpert valve, but which, it is claimed, is easier to construct. The valve closure is made by a metal nose of Monel (instead of Kovar) thrust into a soft copper seat and a larger diameter orifice is used. The body and driver mechanism are of stainless steel and the diaphragm of Monel metal (preferable to Kovar) is 0·004 in. thick. To facilitate soldering in a hydrogen furnace, the stainless steel body is nickel-plated to a thickness of 0·002 in. and a carefully arranged soldering schedule is followed. Molybdenum disulphide—which withstands baking to 400° C *in vacuo*—was used as a lubricant for the valve.

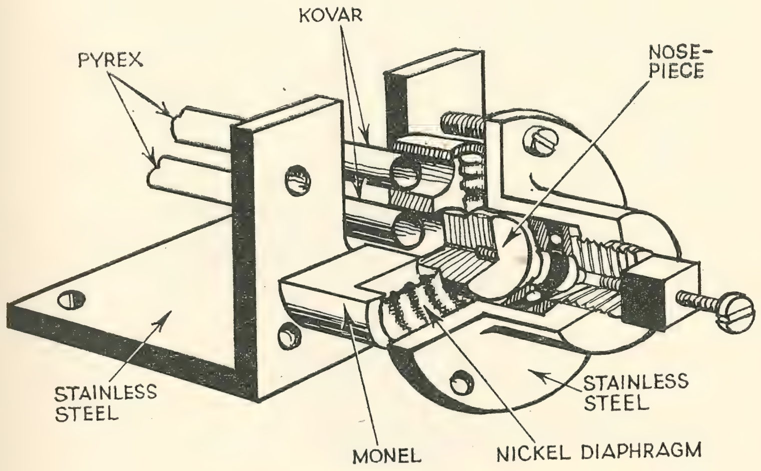


FIG. 5.20 Ultra-high vacuum valve (*Bills and Allen*)

Bills and Allen (BA3) describe a modification of the Alpert valve in which a vacuum-melted pure silver ring is compressed between the Monel nose-piece and the hot-rolled Monel valve body. The silver ring is forced over the nose-piece and then machined to size, the final dimensions being 0·040 in. wide, 0·025 in. thick, bevel angle 45° and a flat-bearing surface of 0·020 in. (Fig. 5.20). An annular groove 0·005 in. wide and 0·010 in. deep, is turned in the valve seat. A nickel diaphragm is used. The assembly including the solder rings (Inconsil-15 flowing at 687° C) and attached to Pyrex-to-Kovar tubes is degreased and then inserted in a hydrogen furnace of the bottle-brazing type (§ 4.3) with the glass tubing clear of the heater coils. The joints are then all soldered simultaneously. The leakage conductance of this valve when closed by a torque of 42·5 lb ft is alleged to be as low as 10^{-14} litre per sec.

5.10. Packless, Glass, Magnetically-operated Valves

Instead of passing the valve stem through the valve bonnet it is possible to dispense with a stem-to-bonnet seal and operate the internal stem by means of an external magnet. This is done in the design by Vogl and Evans (VE1) and also the similar valve described by Yarwood (Y4). A standard spherical ground glass joint is used, the female hemisphere being the valve seat and the male hemisphere the valve 'plate'. The hemispherical 'plate' is raised to open the valve by the action of an external magnet on a cylinder of iron sheet sealed within an attached glass tube. When raised, this movable part is rested upon a dimple within the glass tubing to the vacuum pumps (Fig. 5.21). The hemispherical surfaces are not greased but are ground so as to be a good fit when the valve is closed. Although this means that isolation is not complete, the closed valve yet provides a very high impedance to gas flow. Furthermore, if the valve is made of borosilicate glass it can be baked to 450° C to degas it. It is a useful isolation valve for ultra-high vacuum systems where it can often be used in place of the more elaborate Alpert valve (*see* § 8.3).

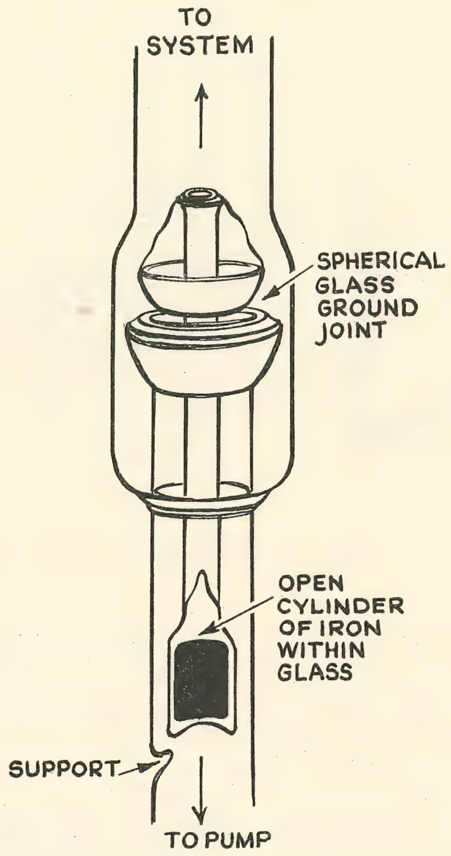

TO SYSTEM
SPHERICAL GLASS GROUND JOINT
OPEN CYLINDER OF IRON WITHIN GLASS
SUPPORT
TO PUMP

FIG. 5.21 A greaseless, glass magnetically-operated isolation valve

Sears and Hopke (SH1) have used a magnetically-controlled cut-off in which a flat quartz plate is held against the ground flat annular surface at the end of a Pyrex tube. Blanaru (B19) has used magnetic control in a valve in which the plate is a Pyrex glass cup filled with tin. This tin is melted by means of an external induction heater coil, the cup raised to the tubular Kovar 'seat', where, on solidification of the tin, a seal is effected (Fig. 5.22). Indium could be used in place of tin. This type of valve bears obvious similarities to the mercury cut-off (§ 5.4), but has the advantages that tin has a very low vapour pressure, even when molten and, furthermore, the final seal is solid, not liquid, and is not liable to disturbance due to pressure differentials.

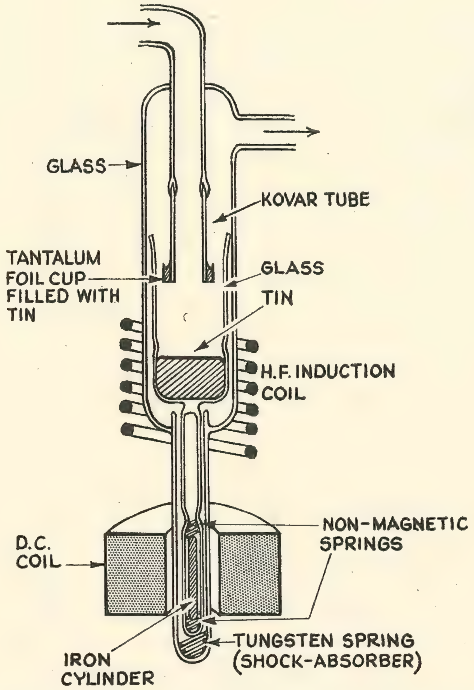


FIG. 5.22 A magnetically-operated valve employing molten tin seal

5.11. Diaphragm Valves

Perhaps the Saunders valve is the best-known example of a valve developed for routine engineering practice which is suitable for vacuum use provided that its seating-surfaces are re-machined. This is a diaphragm valve of the weir type (Fig. 5.23(*a*)) and employs Neoprene sealing. It is not suitable for applications at pressures less than 10^{-3} torr, *i.e.* it is intended for use on the backing side of the vacuum system or where rotary pumps only are employed. Though convenient, widely-used and economical, this type of valve is inclined to give air leakage troubles. It is commercially available (Edward High Vacuum Ltd.) with bore diameters 0·25 to 2 in.

Duncan and Warren (DW1) describe briefly a polythene diaphragm valve (Fig. 5.23(*b*)). The flexible polythene diaphragm *A* is protected by a Neoprene washer I against abrasion by the brass plunger D. On compression of this diaphragm by the plunger, the polythene stud B makes a seat on the end of the polythene tubing C. The metal spring, E, which pushes the stud back when the valve is open, is coated with polythene (§ 4.13). The whole of the valve interior is thus of polythene so that no metal parts are in contact with the gas. The whole valve is welded at J by a nitrogen torch (§ 4.13) after assembly.

A simple **air-admittance valve** of the diaphragm type is shown in Fig. 1.1. Diaphragm valves are also used for gas-metering (§ 5.17).

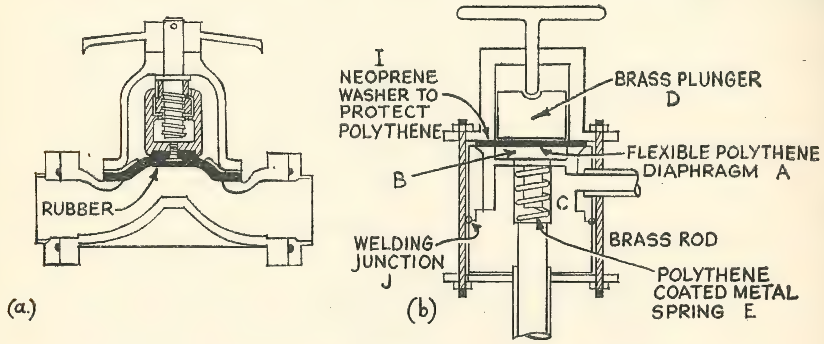

RUBBER
(a.)
I
NEOPRENE WASHER TO PROTECT POLYTHENE
BRASS PLUNGER D
FLEXIBLE POLYTHENE DIAPHRAGM A
B
C
WELDING JUNCTION J
BRASS ROD
POLYTHENE COATED METAL SPRING E
(b)

FIG. 5.23

(*a*) Weir-type diaphragm valve
(*b*) Polythene diaphragm valve

5.12. Gate Valves

Gate valves of the sliding flat-vane type with Neoprene O-ring sealing have been developed in recent years, especially to provide low-impedance isolation valves for vapour pumps. A design due to Wahl, Forbes, Nyer and Little (WFNL1) is illustrated in Fig. 5.24. The vane of this valve is of steel with the surface that slides over the O-ring polished and the leading edge bevelled. The crank is also steel, but the rest of the valve is of brass. To avoid scratching the vane surface, the inner surfaces of the valve body are relieved by 0·005 in. except for strips $\frac{1}{8}$ in. wide at the edges. The Neoprene O-ring that seals against the sliding vane is in a groove of a width of 0·140 in. and a depth of 0·12 in., as measured from the vane surface; it is greased and is chosen to be one size smaller in outer diameter than that normally recommended to reduce the possibility of its being pushed out of its groove on movement of the vane. Valves with apertures of 1 in. and 2 in. dia were built and had a leak rate certainly less than 10^{-5} litre torr per sec for a pressure differential of one atmosphere. Bondelid (B20) gives a design of a similar valve in which the possibility of displacement of the O-ring is reduced by means of inset circular metal pins which are used as spacers to enable the vane to be moved clear of the O-ring until the final half-inch of its motion.

Smith and Seagondollar (SS2) describe a gate valve in which a metal disc containing an off-centre aperture is rotated against a stationary disc on the same axle and also containing a similar aperture. The seal between the two

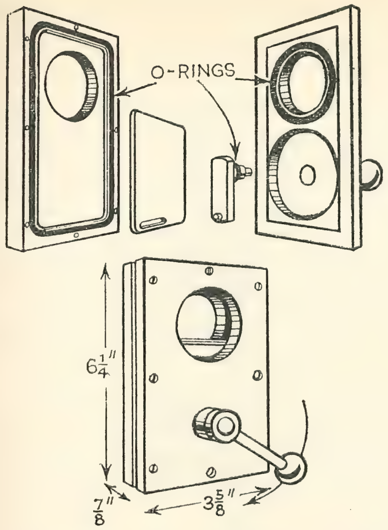


FIG. 5.24 Gate valve of the sliding flat vane type (*Wahl, Forbes, Nyer and Little*)

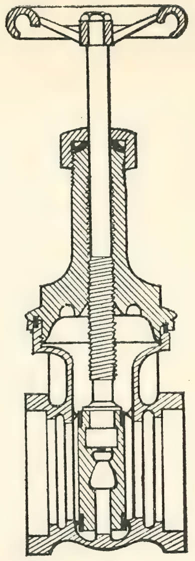
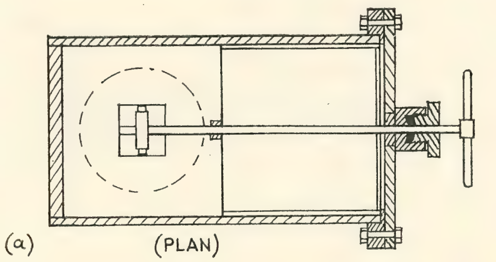
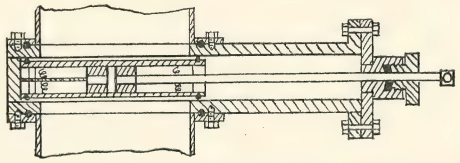


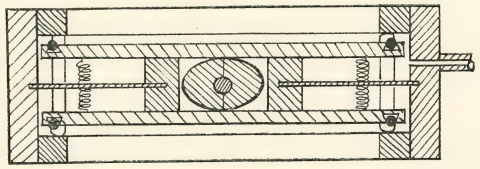
FIG. 5.25 Modification of a Crane gate valve for vacuum use (*Kurie*)



(a) (PLAN)



(b) (VERTICAL CROSS-SECTION)



(c) (VERTICAL CROSS-SECTION PERPENDICULAR TO b)

FIG. 5.26 Gate valve with 8 in. port diameter (*King*)

discs is effected by a Neoprene O-ring under compression; one disc is rotated to align the apertures, *i.e.* open the valve; otherwise a worm-gear drive is used to provide the force necessary to overcome the resistance to motion, due to the friction as the disc slides over the O-ring.

Kurie (K10) describes a modification of a Crane No. 440 brass gate valve (Fig. 5.25) alleged, because of its double disc, to have the virtues of high pumping speed and also suitability as a vacuum lock enabling the insertion of items such as filaments or probes into a cyclotron, for example, with little disturbance of the main vacuum system.

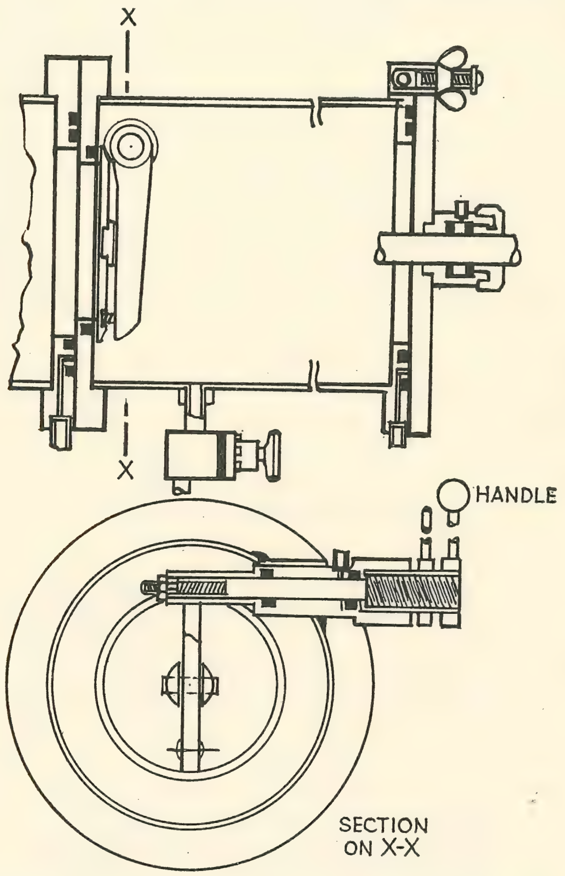


FIG. 5.27 An air-lock with gate valve (*Riddiford and Lilley*)

In a design of a gate valve of 8 in. port diameter, due to King (K11), the gate is maintained in a sealed frame (Fig. 5.26) and consists of two rigid flat surfaces which cover the ports in the vacuum line. To allow free motion in the supporting frame, the plates are normally held together by springs. To close the valve, the gate plates are pushed into the pipe line and then forced apart by the rotation of a cam fixed on the stem which passes through a Wilson seal to outside the valve. O-rings in grooves in the flat gate plates form the seals against the flat surfaces of the pipe-line ports.

This double-seal type of valve has advisedly a small pressure equalizing tube entering the region between the gate plates to prevent the valve from sticking when shut whilst the pressure on both sides is raised above that existing in the valve when it is closed.

Asao and Muramatsu (AM1) describe a modification of King's valve in which all joints between metal plates are made with Neoprene gaskets to avoid soldering or welding. The two gate plates were tapered in this design.

A design of an air-lock with gate valve in which a gate consisting of a hinged flap on a rotatable stem with double O-ring packing due to Riddiford and Lilley (RL2) is shown in Fig. 5.27. Buck (B21) has modified the flap-type gate valve to ensure that it can be opened readily when the atmospheric pressure is forcing the plate against the seat.

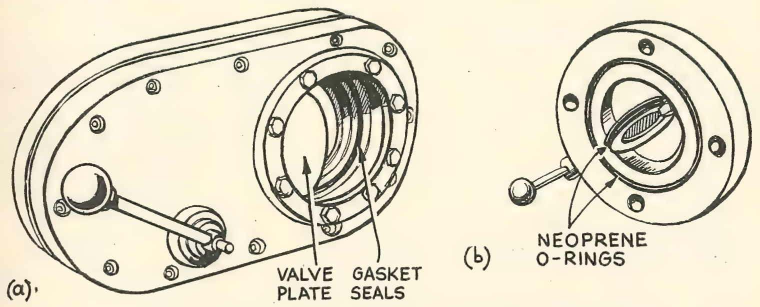


FIG. 5.28 Commercial designs of gate valve

Commercial designs of gate valves are shown in Fig. 5.28. Fig. 5.28(*a*) is an Associated Electrical Industries (Manchester) Ltd. hand-operated sluice valve; an in-line 'butterfly' type valve supplied by Edwards High Vacuum Ltd. (Fig. 5.28(*b*)) has been developed for tubes of 4 in. and 6 in. bore.

5.13. Plug Valves

A metal or glass stopcock (§ 5.3) may be classed as a tapered plug valve. Other designs based on Neoprene O-rings are shown in Fig. 5.29. Shatford's design (S15) of a simple isolation valve (Fig. 5.29(*a*)) has been made in a number of sizes for pipe-line bores of $\frac{1}{4}$ in. to 1 in.; its construction can be understood from the diagram. In his two-way plug valve design (Fig. 5.29(*b*)), movement of the plunger to the left or right will open a passage from port *A* to *B* or *C* respectively. Vacuum grease is used on the O-rings. Green (G10) gives a simple construction of a plug valve with an $\frac{1}{2}$ in. bore (Fig. 5.29(*c*)). The cylindrical brass body *B* is turned from the solid, a brass tube *A* is passed through the opposite apertures in the wall of *B* and hard-soldered in position. The centre of this tube *A* (*i.e.* within the valve body) is then removed by boring, leaving two short stubs which project by about three-quarters of the uncompressed thickness of the O-rings. The duralumin plug *C* is an easy fit between the stubs; the edges of the hole in the plug must be radiused to prevent cutting of the O-rings. All the O-rings are lubricated with Apiezon J oil.

Barrow (B22) describes a plug valve used as a simple air-lock so that an ionization gauge may be fitted and removed without losing the vacuum in, for example, a large proton-synchrotron.

Moore (M10) has designed a tapered plug valve using O-rings in a modified large steel conical valve (taper 1 in 5).

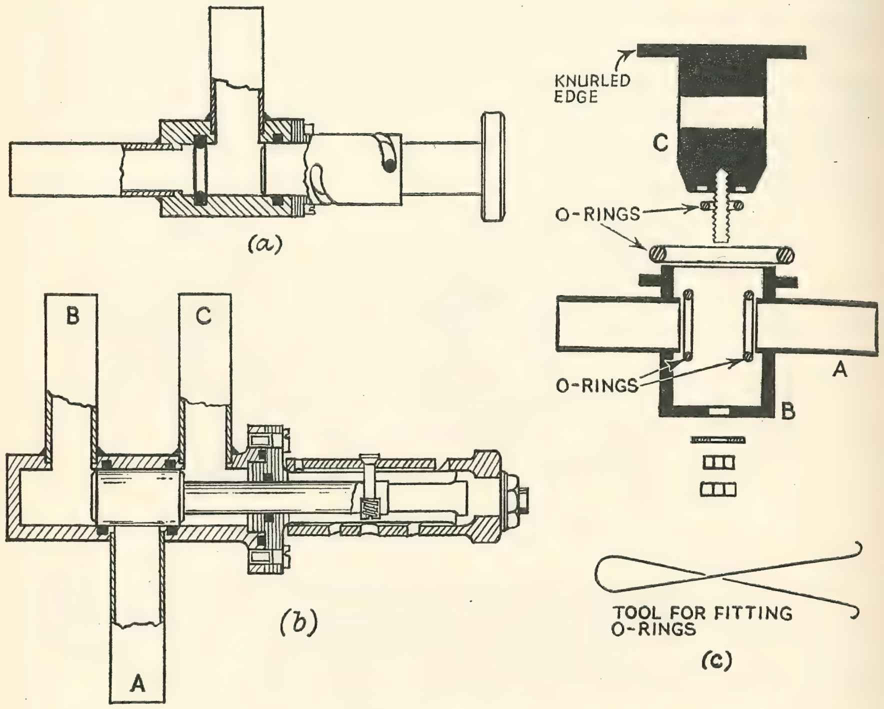


Fig. 5.29 Plug valves

5.14. Multiple Valve Units

Multi-purpose vacuum valve blocks for vacuum systems are a feature of some large plants, and are especially favoured in German practice. The chief disadvantage is that the necessarily costly multiple valve is more difficult to repair if it becomes faulty. The outstanding advantage is that routine operation of the vacuum plant by unskilled personnel is facilitated. Leybold describes a valve block in which the following valves are coupled mechanically and the connecting lines are within the block (Fig. 5.30(*a*)).

Valve 1: isolates the vacuum tank from the vapour pump.
Valve 2: isolates the rotary pump from the vacuum tank so long as it is not working as a roughing pump but as a fore-pump to the vapour pump.
Valve 3: a valve between the vapour pump and the rotary pump.
Valve 4: an air-inlet valve to the vacuum tank.

The valve-operating handle can only be turned in one direction (Fig. 5.30(*b*)) so that the correct sequence of operation of the valves is automatically

achieved. The removal of a locking catch enables the handle rotation to be reversed, if required. The air-inlet valve can only be opened when the valves between the pumps and the container are closed.

Garrod and Coyle (GC1) give a detailed diagram of a multiple valve in which three valves (the isolation valve between the vapour pump and the vacuum tank is separate) are opened or closed by two specially-shaped cams rotated on a common handle-driven shaft so that operations are performed in the following sequence: during the first 120° of rotation of the valve handle, the vapour pump is isolated from the rotary pump, the air inlet is closed and the vacuum tank is pre-evacuated by the rotary pump through a line (within the valve body) which by-passes the vapour pump; when the tank pressure is sufficiently low, further rotation through 120° of the valve handle causes the valve between the rotary and vapour pump to open. The independent large valve between the vapour pump and the tank is then opened. Finally to admit air to the system, the independent valve is closed and rotation of the handle of the multiple valve through an extra 120° opens the air-admittance valve.

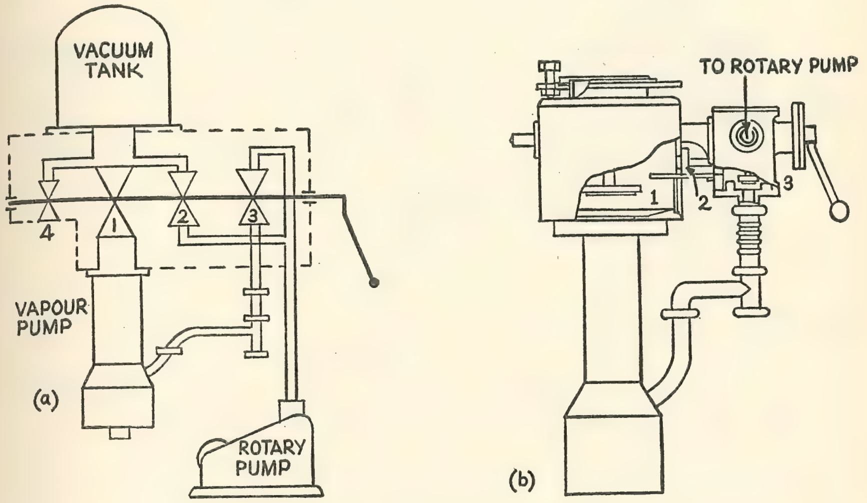


Fig. 5.30 A Leybold valve block and its functions

5.15. Electrically-Operated Isolation Valves

It is of great importance in many types of complex vacuum systems to be able to operate the valves automatically or semi-automatically. If the opening and/or closing of a valve can be controlled by the passage of an electric current then three benefits may be gained: first, the valves can be operated from a position remote from the vacuum plant and a correct sequence decided by electric switches, which, if desired, can be interlocked; second, the supply of electric power to some essential part of the vacuum plant (*e.g.* the rotary pump motor) can also be used to operate the valve so that protective devices, *e.g.* against failure of electric current supply, can be incorporated; thirdly, the valve can be opened or closed at a pre-determined pressure monitored by an electrical type of vacuum gauge such as a thermocouple gauge, a Pirani gauge, an ionization gauge or even a simple discharge tube.

A range of magnetic valves is marketed by Edwards High Vacuum Ltd. The typical principle adopted is shown in the self-explanatory diagram of Fig. 5.31. These valves are maintained closed magnetically against a spring which opens the valve to the atmosphere when the current is cut off.

The range of such valves includes magnetic air-admittance valves of $\frac{1}{16}$ in. and $\frac{1}{8}$ in. bore, designed to admit air automatically to the rotary pump when it is switched off—either deliberately or inadvertently—so that oil is not sucked back into the connecting pipe line; magnetic isolation valves of $\frac{1}{2}$ in. and 1 in. bore; and magnetic valves of $\frac{1}{2}$ in. and 1 in. bore combining isolation and air admittance which incorporate an auxiliary valve to admit air to a rotary pump on switching off whilst the main valve isolates the pump from the system (the valve can be wired to operate from the pump motor switch); also magnetic isolation valves of 2 in. bore, one design is water-cooled and intended for use as a baffle isolation valve on a vapour pump, the other is a general purpose valve. Typical applications of these valves are shown in Fig. 5.31(*b*) and a rectifier circuit for operation from an a.c. mains supply is shown in Fig. 5.31(*c*).

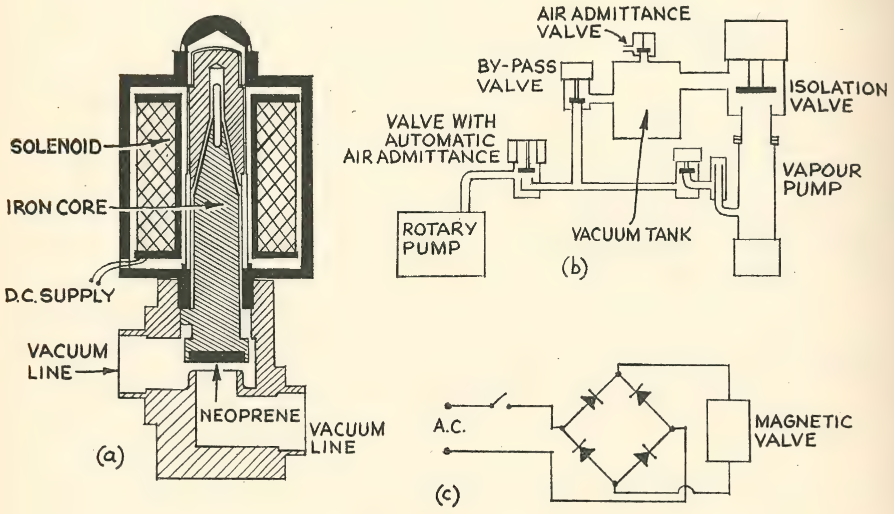


FIG. 5.31

(*a*) Magnetically operated isolation valve (*Edwards High Vacuum Ltd.*)
(*b*) Typical uses of magnetic valves.
(*c*) Electric circuit for operation of magnetic valve from a.c. mains supply

Electric vacuum valves are also supplied by Associated Electrical Industries (Manchester) Ltd. and by N.G.N. Electrical Ltd.

An electro-pneumatic valve designed to protect the vacuum system of a Van de Graaff generator against rotary-pump drive failure is described by Green (G11). A small, solenoid-operated valve *A* (Fig. 5.32) is kept closed by current from a small d.c. generator coupled to the rotary–pump driving belt. Air is admitted to the chamber *B* if the pump ceases to rotate; the sylphon bellows *C* are thus compressed to force the rubber-faced disc *D* against the pump-line port, so isolating the pump from the system. A small leak *E* allows the interior of the pump to rise to atmospheric pressure, preventing oil suck-back. As the differential pressure across the bellows falls, the pressure on the disc *D* is increasing due to the atmosphere. On restarting the pump, the operation sequence is reversed.

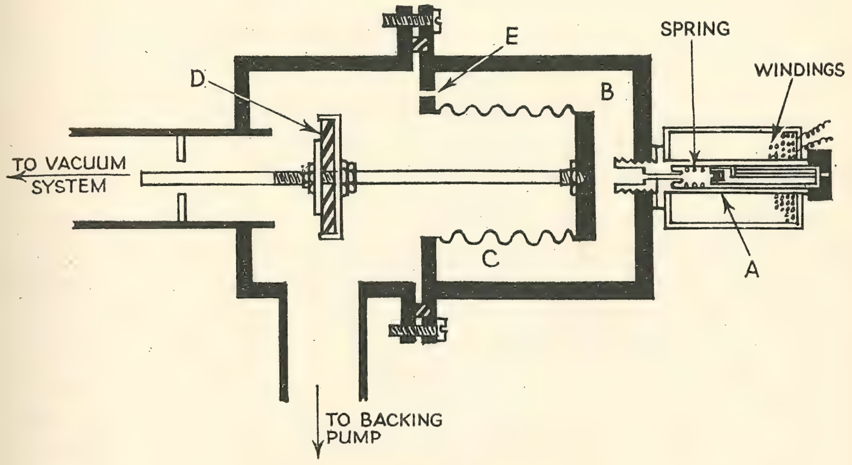


FIG. 5.32 An electro-pneumatic valve (*Green*)

In an automatic valving system for an electron microscope due to Felheimer and Litwak (FL1) basically automatic control was derived by the current developed in a discharge tube at a pre-determined pressure which operated a relay. Motorized valves were preferred to solenoid-operated ones because the latter open or close instantaneously, whereas a gate type valve (§ 5.12), with an electric motor-driven stem can be operated slowly and allow the vacuum pump to pick up under slowly changing loads.

Gate valves of the sliding-vane type with bore diameters of 4 in., 6 in., 10 in. and 16 in., and which can be operated manually, by an electric motor or by compressed air, are marketed in Britain by Vacuum Metallurgical Developments Ltd.

5.16. Compressed-air Operated Valves

As an alternative to electric operation, compressed air operation is often convenient. The drive for gate valves of the sliding-vane type can be arranged in this way. A small compressed air valve made by Edwards High Vacuum Ltd. is shown in Fig. 5.33(*a*). The valve is normally held open by a helical spring; compressed air supplied to the chamber *C* of the valve closes it. A large electro-pneumatic gate valve made by the Vacuum Research Co. is illustrated in Fig. 5.33(*b*).

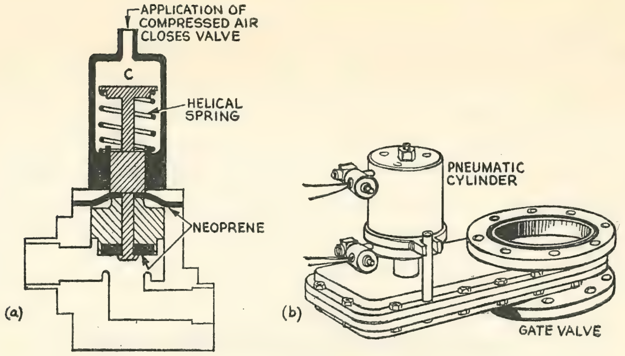


FIG. 5.33 Compressed-air operated valves

5.17. Gas-metering Devices

The need to admit gas at a controlled rate into an evacuated enclosure is often encountered. In the authors' experience, small flow rates are best arranged by the use of an Alpert-type ultra-high vacuum valve, especially when the initial pressure is 10^{-6} torr or less and it is required to let in gas to a pressure of not more than 10^{-5} torr. Indeed, this valve seems to be the only satisfactory general purpose device whereby, for example, a vessel may be filled with a known gas at a pressure of 10^{-9} to 10^{-5} torr. Indeed, for many applications, such as the gas-filling of electronic tubes at low pressures, in the usual arrangement of two glass greased taps separated by a capillary tube of known volume, the taps are best replaced by Alpert valves. This avoids the use of troublesome grease, enables the valves to be degassed by baking and also allows the associated glass or metal tubing to be baked either in an oven or by thermal tapes.

As a coarser gas-metering device, the **needle valve** may be used. An early pattern is due to Le Rossignol (L9) who made the body of the valve from bronze and the needle from nickel alloy to reduce rusting and corrosion, features unfortunately not considered in some modern needle valves. Figure 5.34 shows two typical more recent designs. Figure 5.34(*a*) illustrates a model supplied by Edwards High Vacuum Ltd.; Fig. 5.34(*b*) is a readily-constructed design due to Alexander (A8). As they employ Neoprene sealing, these valves cannot be baked. They are inclined not to give reproducible readings and exhibit backlash. It is difficult to use a needle valve of these types to admit air directly from the atmosphere to an evacuated vessel unless pressures of at least 10^{-3} torr are required. In fact, it is recommended that to meter-in gas to pressures of less than 10^{-3} torr, the inlet to the needle valve should be connected to a reservoir of the gas at reduced pressure, say 1 torr.

Kersten and Lange (KL1) describe a bellows-sealed needle valve of which the needle (a large darning needle is used) is driven by a reduction worm-gear so that one turn of the worm will move the needle 0·0005 in. A later design due to Kersten (K12) employs a differential screw drive for the needle. Edwards and Maxwell (EM1) give a design more suitable for general vacuum work (Fig. 5.35(*a*)) in which, as in the models illustrated in Fig. 5.34, a long, slightly tapered needle seats into a carefully ground tapered hole. Sylphon bellows sealing is used and a spring ratchet device prevents the use of excessive force in seating the needle, which might well damage both the needle and the seat. A small flange on the valve stem limits the bellows compression. This valve was made of brass, but could be of copper or stainless steel and, though not mentioned by the author, could presumably be baked to some extent to degas it. It is reported to be conveniently adjustable to give a leak of 10^{-3} litre torr per sec from a source at atmospheric pressure. Topanelian and Coggeshall (TC1) also give a design of a bellows-sealed needle valve which is primarily intended as a small greaseless valve for use in place of a greased stopcock (Fig. 5.35(*b*)). Babelay and Smith (BS3) describe a needle valve which provides a very wide range of flow rates and can also be shut off completely; it is a modification of a standard Hook 411 type of needle valve. A fine control valve of the needle type with a polytetrafluoroethylene stem and needle is described by Duncan and Warren (DW1), the packing of the stem being in the form of a double Wilson seal (Fig. 5.36).

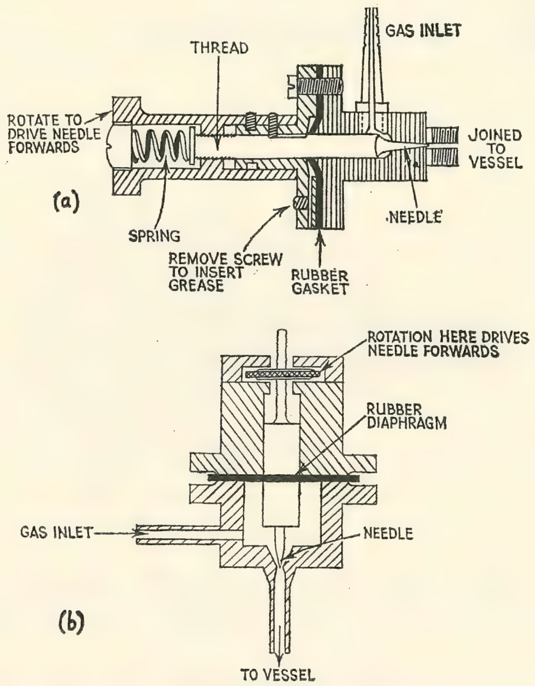


FIG. 5.34 Designs of needle valve

As an alternative to the needle valve, a **variable capillary leak** or a **diaphragm-type flow control valve** may be used. Fowler has used a U-shaped silver tube which is flattened over part of its length and which is flexed by a screw adjustment to alter the close separation between the flattened tube walls and so the gas conductance of the tube. Nier, Ney and Ingham (NNI1) have developed

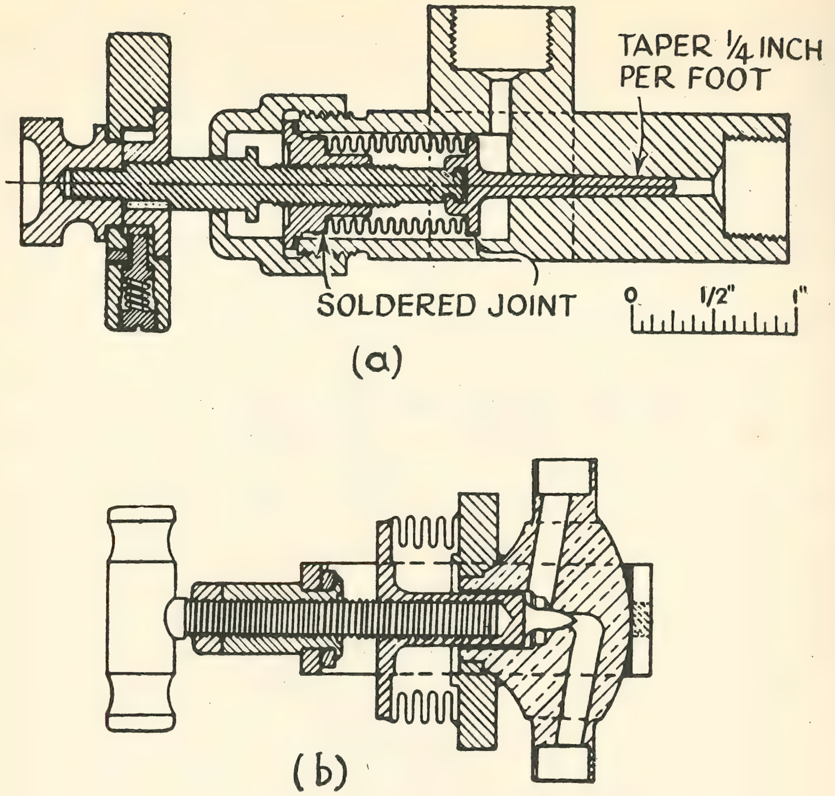


FIG. 5.35

(*a*) Bellows-sealed needle valve (*Edward and Maxwell*)
(*b*) Bellows-sealed needle valve (*Topanelian and Coggeshall*)

the Fowler technique by using as an adjustable gas leak a piece of copper tubing (length 12 in.; O.D. 0·125 in.; wall thickness 0·025 in.) bent to a hairpin shape which is then flattened for a distance of 2·5 in. back from the apex of the hairpin between jeweller's rollers. The apex of the hairpin is then silver-soldered to a steel shaft and the flattened tubing is wrapped approximately three times around this shaft. The shaft is turned by a worm-gear to vary the gas conductance of the flattened tube (Fig. 5.37). The leak rate could be varied over a range of 100 and, in some cases, 1000, but the gas flow could not be cut off entirely.

Halban and Wilson (HW2) have used a modification of a Saunders diaphragm valve as a simple tap and gas flow controller. Bowring and Davies (BD1) used Hycar E75 (Gaco) material of $\frac{1}{16}$ in. thickness or Neoprene as the diaphragm materials in an improved version of the Halban and Wilson valve.

The regulation of the gas flow into a vacuum system may also be achieved by the **use of a porous solid**, *e.g.* porcelain. Several techniques of this kind have been developed. Dorn and Glockler (DG1) describe a device in which the length of surface of a porous porcelain tube through which gas permeates is varied by altering the height of a surrounding column of mercury. Smythe (S16) used an unglazed porcelain capillary tube (length 8 cm; I.D. 0·8 mm; O.D. 1·5 mm) which seals to Nonex glass. The device for raising and lowering the mercury level about this tube is illustrated in Fig. 5.38(*a*). By turning the nut *N*, the capacity of the mercury reservoir is varied and the mercury in the capillary is raised or lowered. Bazzoni (B23) has introduced a modified and simpler form of the Smythe adjustable leak in which a rubber medicine dropper bulb is used to vary the height of the mercury. Glaister (G12) used a slightly convex sintered glass disc *D* (Fig. 5.38(*b*)) just beneath the surface of a pool of mercury in which a soft iron cylinder *C* floats. On lifting this iron cylinder clear of the mercury by switching on the current in the external solenoid, the mercury level falls to just that amount required to leave the sintered disc surface clear; gas then permeates the disc, *i.e.* the valve is opened. To prepare the sintered glass disc, 80-mesh powdered Hysil glass was placed

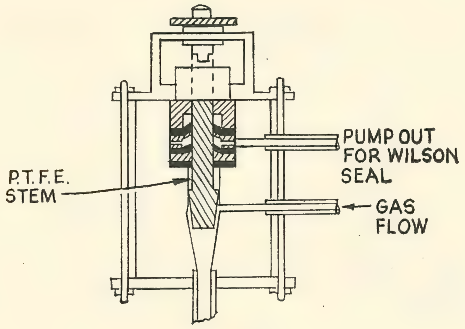


FIG. 5.36 A fine control valve with a polytetrafluoroethylene stem (*Duncan and Warren*)

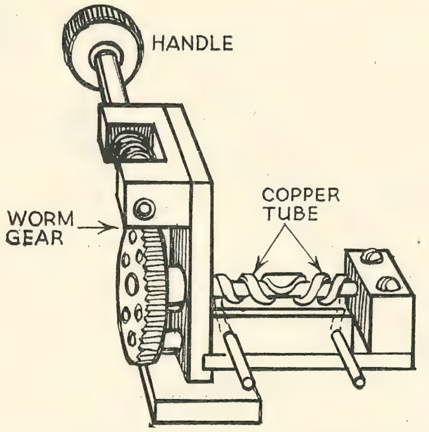


FIG. 5.37 An adjustable gas leak (*Nier, Ney and Ingham*)

to a depth of 5 mm in a graphite mould. This was heated by an induction heated until coalescence began to occur when the disc was pressed to a thickness of 3 mm.

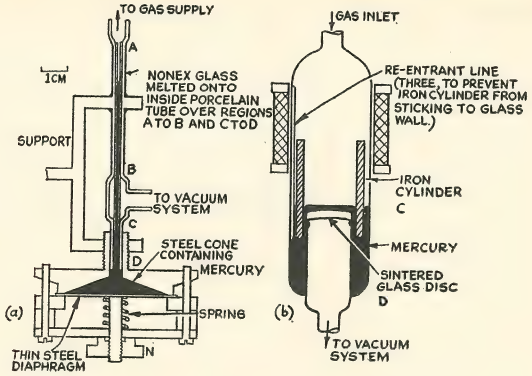

TO GAS SUPPLY
A
1CM
NONEX GLASS MELTED ONTO INSIDE PORCELAIN TUBE OVER REGIONS A TO B AND C TO D
SUPPORT
B
TO VACUUM SYSTEM
C
D
STEEL CONE CONTAINING MERCURY
SPRING
(a)
THIN STEEL DIAPHRAGM
N
GAS INLET
RE-ENTRANT LINE (THREE, TO PREVENT IRON CYLINDER FROM STICKING TO GLASS WALL.)
IRON CYLINDER
C
MERCURY
SINTERED GLASS DISC
D
(b)
TO VACUUM SYSTEM

FIG. 5.38
(*a*) An adjustable vacuum leak (*Smythe*)
(*b*) A magnetically-controlled gas leak device (*Glaister*)

Instead of using a porous tube, Leemans (*private communication*) has developed for general gas admittance the use of a glass tube with a longitudinal crack in its wall, originally employed by Kunzl and Slavic for air admittance. The length of the crack through which gas passes is varied by controlling the height of a mercury column in a surrounding tube. A piece of borosilicate glass tubing 6 cm long is scratched internally over the full length, using a diamond mounted near the end of a $\frac{3}{16}$ in. steel rod. The crack starts spontaneously and is chased along the outside of the tube with a small gas-air flame. As this crack did not usually penetrate the glass wall fully, a simple tool was devised, one end of which could be inserted in the glass tube end and then

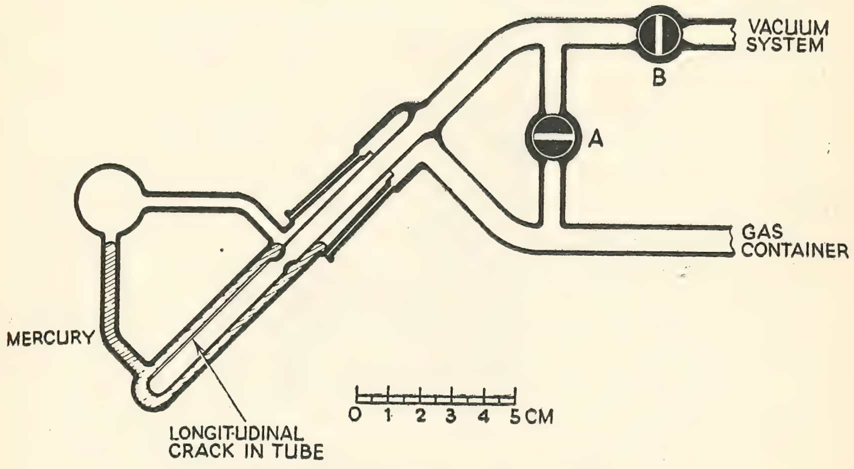

VACUUM SYSTEM
B
A
GAS CONTAINER
MERCURY
LONGITUDINAL CRACK IN TUBE
0 1 2 3 4 5 CM

FIG. 5.39 Leemans gas dispenser

expanded slightly. To vary the height of the mercury column around the cracked tube, the dispenser (Fig. 5.39) is turned about an axis perpendicular to the plane of the diagram. In operation, the tap *A* is closed after evacuation and then connection is made to the reservoir of gas. Tap *B* must be closed before the vacuum system is opened to the atmosphere, otherwise, if the pressure in the gas reservoir is below atmospheric, air will bubble through the crack and the mercury into this reservoir. If, however, the dispenser is used solely to admit air, the two taps may be omitted. A similar arrangement could be developed using a sintered glass or porous porcelain tube in place of the longitudinally cracked tube.

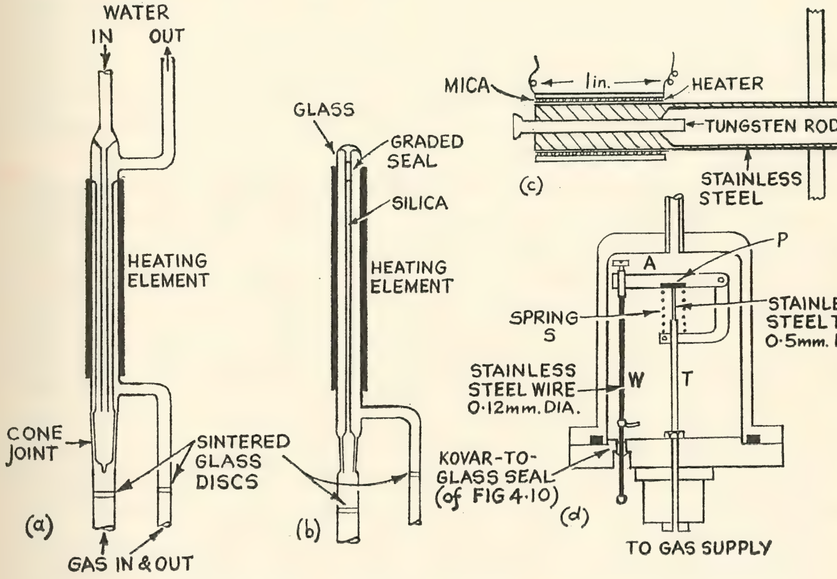

WATER
IN
OUT
HEATING ELEMENT
CONE JOINT
SINTERED GLASS DISCS
(a)
GAS IN & OUT
GLASS
GRADED SEAL
SILICA
HEATING ELEMENT
(b)
MICA
1 in.
HEATER
TUNGSTEN ROD
STAINLESS STEEL
(c)
P
A
SPRING S
STAINLESS STEEL TUBE 0·5mm. I·D.
STAINLESS STEEL WIRE 0·12mm. DIA.
W
T
KOVAR-TO-GLASS SEAL (cf FIG 4·10)
(d)
TO GAS SUPPLY

FIG. 5.40 Gas-flow control valves which utilize thermal expansion

Jenkins (J6) makes use of a plug of porous metal to construct a constant leak. The bore of a hole in a mild steel block is first tinned in soft solder and then soft solder powder (a washed proprietary solder paste is satisfactory) is compressed into the hole. By varying the degree of compression (arranged by applying pressure to the solder whilst it is temporarily between a flat plate and an inserted metal plug) various sizes of leak can be made.

Mercury-in-glass devices for introducing small metered quantities of gas into a vacuum system, as used, for example, in gas adsorption studies, are described by Mignolet (M11) and Wyllie (W4 and W5).

Harrison (H15) has designed a greaseless valve for controlling gas flow which is actuated by the **differential expansion of dissimilar metals** or of similar materials at different temperatures. It can handle several corrosive gases and is also controllable electrically from a remote position, if desired. In the design shown in Fig. 5.40(*a*), raising the temperature of the outer tube causes differential expansion to occur in an axial direction so that the male cone is withdrawn slightly from the female cone. These conical (or hemispherical) glass joints are carefully ground to a good fit but are not greased. The gas-flow rate is controlled by adjusting the temperature difference between the inner tube (water-cooled) and the outer tube (electrically heated). Fig. 5.40(*b*) shows a construction in which the inner tube is of silica which is connected to the outer tube of borosilicate glass through a graded seal. The difference between the thermal expansion coefficients of silica and glass now create the necessary movement of the male cone from the female cone. Sintered glass filter discs in the inlet and outlet tubes of these devices prevent the entry of dust and other solid particles. The rate of flow of gas can be calibrated in terms of the voltage applied to the heating element which, in each case, consists of a Nichrome wire wound on a layer of asbestos paper on the outer tube and covered with asbestos tape. The shut-off rate of flow for the valve of Fig. 5.40(*b*) was 5×10^{-4} litre torr per sec. For the valve of Fig. 5.40(*a*), the rate of flow of air could be varied by a ratio of about 100 for a change of temperature of the outer tube from 20° to 400° C.

Green (G13) has also made use of the differential expansion of two materials to construct an all-metal control valve (Fig. 5.40(*c*)). It consists of a stainless steel tube into which is shrunk a tungsten rod so that, at room temperature, the valve is closed. The tungsten rod was ground 0·0002 in. over the size of the bore in the stainless steel tube and then inserted on heating this outer tube. The heater consisted of a single layer of 0·0625 in. × 0·005 in. Nichrome tape wound over the stainless steel tube but insulated from it by thin mica strips and covered over on the outside with asbestos tape.

Flinta (F8) gives a design of a gas leak in which control is arranged by varying the temperature and hence the length of a wire (Fig. 5.40(*d*)). A movable arm *A* carries a rubber pad *P* which bears on the opening of the vertical gas supply tube *T*. The stainless steel wire *W* holds this pad tight against the opening, and acts against the spiral spring *S* which pushes upwards against the arm *A*. On heating the wire *W* by electric current, it expands, the spring raises the arm slightly and gas is admitted via the supply tube *T*. The leak rate depends on the power supplied to the wire.

Jossem (J7) makes use of the **permeation of gas through a heated metal** tube to control the flow rate into a vacuum system. Hydrogen may be introduced through a heated palladium or platinum tube; oxygen through silver, nickel or copper; nitrogen through molydenum, iron or chromium; carbon dioxide through iron or nickel; whilst for helium or other rare gases, a heated clear quartz tube may be used. Jossem heated the appropriate metal tube by a surrounding wire carrying a regulated electric current. Leemans (L17) has used the town coal-gas supply as a source of hydrogen and has devised a simple arrangement in which a palladium osmosis tube is heated by the ignited gas escape jet.

6

SORPTION AND DESORPTION OF GASES AND VAPOURS BY SOLIDS: CLEAN-UP

6.1. Terms Used

The taking-up of gas or vapour by a solid is known as **sorption**, the verb being 'to sorb'. The opposite process, *i.e.* the giving-up of a gas or vapour by a solid, is **desorption**, the verb being 'to desorb'. There are two main classes of sorption phenomena: **adsorption**, in which the gas or vapour is taken up at the surface of the solid, and **absorption** where the gas or vapour is taken up within the molecular structure of the solid. If chemical combination takes place between the gas or vapour and the surface or the interior of the solid, a special type of sorption, known as **chemisorption** is concerned. In vacuum technology, the most widely practised sorption technique in the production of low pressures is that of **gettering**. A **getter** is a material which is included within a vacuum system or vacuum tube for sorption of the residual gases and vapours.

The term **clean-up** is often used to denote the removal of gas both by sorption and/or by ion pumping. In this text, the term **electrical clean-up** will be used to denote ion pumping, *i.e.* a process in which some of the residual gas in a vacuum system or device is ionized and some of these ions are driven (by the action of an electric field) to electrodes or the inner surfaces of the containing vessel where, depending on the circumstances, all or a fraction of them will be retained, so reducing the pressure in the container. In practice, however, electrical clean-up cannot sometimes be distinguished satisfactorily from other sorption processes (§ 6.14).

Sorption and Desorption of Gases and Vapours by Constructional Materials

6.2. Adsorption

The interior surfaces within a vacuum system will both sorb and desorb gases and vapours. In general, surfaces which have not been degassed by heating or by electron or ion bombardment will act as sources of gas rather than as sinks. Sorption of the residual gases by constructional materials is primarily of importance, therefore, subsequent to bake-out or other degassing procedure.

In practice, adsorption and absorption will often both take place simultaneously so that it is not readily possible to distinguish between them experimentally except in certain special cases. True physical adsorption results in bound surface layers of molecules of not more than one or two molecules in thickness. In general, the finely-divided solids will adsorb gases in large amounts because of the large effective surface area they present. Adsorption proper increases with decrease in temperature of the surface and, in general, is greater at a given temperature for the more readily condensable gases, of which water vapour is particularly important. It is frequently observed, however, that the amount of gas sorbed decreases with temperature to a minimum and then is subject to a reversal because of chemisorption (Dushman, D1).

The number of molecules, N_S, constituting a monolayer on a surface of one sq cm in area can be calculated from a knowledge of the size of the molecule of the gas in question, assuming that the molecules are stacked side-by-side on the surface. Table 6.1 is based on data given by Dushman (D1); also included is the corresponding volume, V_{20}, of gas in cm^3 at 20° C and 760 torr.

TABLE 6.1

The number of molecules, N_S, in a monolayer per cm^2 of smooth surface and the corresponding volume of gas, V_{20}, in cm^3 at 20° C and 760 torr

Gas (in molecular form)	N_S	V_{20} in cm^3
Hydrogen	$15{\cdot}2 \times 10^{14}$	$6{\cdot}1 \times 10^{-5}$
Helium	$24{\cdot}2 \times 10^{14}$	$9{\cdot}7 \times 10^{-5}$
Argon	$8{\cdot}5 \times 10^{14}$	$3{\cdot}4 \times 10^{-5}$
Nitrogen	$8{\cdot}1 \times 10^{14}$	$3{\cdot}2 \times 10^{-5}$
Oxygen	$8{\cdot}7 \times 10^{14}$	$3{\cdot}5 \times 10^{-5}$
Carbon monoxide	$8{\cdot}1 \times 10^{14}$	$3{\cdot}2 \times 10^{-5}$
Carbon dioxide	$5{\cdot}3 \times 10^{14}$	$2{\cdot}1 \times 10^{-5}$
Water vapour	$5{\cdot}3 \times 10^{14}$	$2{\cdot}1 \times 10^{-5}$

It is, however, not readily possible to apply these figures in practice to calculate the volume of gas adsorbed in a particular case because the layer may be one or two molecules thick and, of greater importance, the true surface area of the solid is often considerably different from the apparent area. Moreover, this ratio of the true to apparent surface area is not constant for a given material but depends markedly on its structure and on its previous history. For example, in the case of nickel, figures given by McBain (M12) for the ratio of true to apparent surface area are 75 for newly-polished nickel, 9·7 for old-polished nickel and 46 for nickel which has been activated by alternate oxidation and reduction.

The number of molecules, N, which impinge on a surface of unit area per sec is given by (*see* Appendix A):

$$N = \tfrac{1}{4}\, n\bar{v}$$

where n is the number of molecules per unit volume in the gas adjacent to the surface and $\bar{v}$ is the average velocity of these molecules. This expression can be put in the alternative form (*see* Appendix A)

$$N = \frac{3{\cdot}5 \times 10^{22}\, p}{\sqrt{MT}} \text{ per sq cm per sec} \qquad (6.1)$$

where p is the gas pressure in torr and M is the molecular weight of the gas.

For a temperature of 20° C, *i.e.* 293° K, this becomes:

$$N = \frac{3{\cdot}5 \times 10^{22}}{\sqrt{293}}\,\frac{p}{\sqrt{M}} = \frac{2 \times 10^{21}\, p}{\sqrt{M}} \qquad (6.2)$$

The time t required to form a monolayer is given by:

$$t = \frac{N_S}{N} = \frac{N_S\sqrt{M}}{2 \times 10^{21}\, p} \qquad (6.3)$$

For nitrogen, $M = 28$ and $N_S = 8{\cdot}1 \times 10^{14}$ (Table 6.1), therefore

$$t_{\text{nitrogen}} = \frac{8{\cdot}1 \times 10^{14}\,\sqrt{28}}{2 \times 10^{21}\, p} = \frac{2{\cdot}14 \times 10^{-6}}{p} \text{ sec} \qquad (6.4)$$

It follows that a monolayer will form in a time of just over 2 sec at a pressure of 10^{-6} torr. Except in ultra-high vacua ($p < 10^{-7}$ torr) all surfaces will normally be covered with monolayers. Even at very low pressures, say 10^{-9} torr, a monolayer would form in roughly 2000 sec, but then there are often not enough molecules within the container to make up a full monolayer. For example, at 10^{-9} torr, a one-litre vessel contains about $3{\cdot}5 \times 10^{10}$ molecules of gas (*see* Appendix A) whereas a complete monolayer on a surface of area 1 cm^2 comprises about 10^{15} molecules.

6.3. The Sorption of Gases by Metals

In many cases, adsorption is accompanied by chemisorption, which will increase in rate with temperature, leading to the formation of, for example, oxide, hydride or nitride surface films of 10^{-6} to 10^{-4} cm in thickness. Furthermore, metals may also absorb gas into solution so that the gas molecules incident on the metal surface diffuse into the interior, where they are retained. The dissolved gas content will depend on the nature of the metal, the metallurgical process used in the production of the metal and the pre-treatment (including degreasing, cleaning and storing *in vacuo* or in a hydrogen atmosphere) to which the metal is subjected. So far as is known, the inert rare gases do not dissolve in (or permeate through) any metal at any temperature.

The interaction with and solubility of gases in metals is fully discussed from the point of view of vacuum technique by Dushman (D1) on whose text the following abbreviated data is largely based.

Hydrogen. Four types of interaction between hydrogen and metals are:

(*a*) the alkali and alkaline-earth metals form hydrides;

(*b*) elements like arsenic, selenium and silicon, and the more distinctly non-metallic elements carbon and sulphur, form covalent hydrides, *e.g.* AsH_3, SiH_4 and H_2S;

(*c*) several metals, *e.g.* aluminium, chromium, cobalt, copper, iron, molybdenum, nickel, platinum, silver and tungsten, dissolve hydrogen to form true solutions; this solubility *increases* with temperature and with $p^{\frac{1}{2}}$, where p is the superincumbent pressure of hydrogen; the dissolved gas is here in the *atomic* not the molecular state.

TABLE 6.2

Solubility *s* (in cm³/100 g) of hydrogen at 760 torr in metals for which true solutions are formed

Metal	Temperature in °C														
	200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600
Aluminium						0·15	0·49	1·48							
Chromium					0·5		1·0	2·0	3·0	4·2					
Cobalt					0·89	1·22	1·85	2·52	3·21	4·33	5·44				
Copper			0·06	0·16	0·30	0·49	0·72	1·08	1·58	6·3	8·1	10·0	11·8		
Iron		0·16	0·35	0·75	1·20	1·85	2·45	3·0[1]	5·5	7·0	8·25	10·1	10·5[2]		28
								4·7[2]					10·1[3]		
Molybdenum			0·165	0·175	0·185	0·21	0·25	0·29	0·50	0·62					
Nickel	1·70	2·35	3·15	4·10	5·25	6·50	7·75	9·10	9·80	12·15	14·25	14·7	16·2	41·6	
Platinum			0·065		0·075		0·095	0·135	0·20	0·35	0·52	0·77	1·15		
Silver			0·055	0·110	0·176	0·232	0·334	0·427							

[1] Iron in α-phase: body-centred cubic crystal; range of stability up to 906° C.

[2] Iron in γ-phase: face-centred cubic crystal; range of stability 906° to 1403° C.

[3] Iron in δ-phase: body-centred cubic crystal; range of stability 1403° to 1537° C.

(*d*) the metals colombium, hafnium, palladium, tantalum, thorium, titanium, vanadium and zirconium behave peculiarly in that they form pseudo-hydrides when in contact with hydrogen where the solubility depends on $p^{\frac{1}{2}}$ for certain ranges of values of the superincumbent pressure *p*, but where *decrease* of solubility occurs with temperature rise.

The solubility *s* is usually expressed in cm³ of gas at one atmosphere (760 torr) per 100 g of metal. For metals within the category (*c*) the values of *s* for hydrogen are much less than those for metals in category (*d*). Table 6.2 gives the values of *s* for hydrogen in the former class of metals at various temperatures; Table 6.3 gives the values for the latter class of metals (both tables are based on data compiled by Dushman, D1).

TABLE 6.3

Solubility *s* (in cm³/100 g) of hydrogen at 760 torr in metals for which pseudo-hydrides formed; values of *s* much larger than those in Table 6.2

Metal	Temperature in °C										
	200	300	400	500	600	700	800	900	1000	1100	1200
Colombium	5,500	4,440	3,680	2,270	988	511	330	217	163		
Palladium	6,000	330	230	190	180	170	162	157	155	154	
Tantalum	4,600	3,300	2,500	1,400	700	420	250	180	140	110	100
Thorium	14,800				9,100	8,800	8,100	7,700	2,600	1,900	1,756
Titanium	40,740		38,770	36,600	33,470	18,390	14,090	9,820	6,610	4,590	
Vanadium	15,000	6,500	3,800	1,900	1,000	640	440	320	250	210	
Zirconium	23,550				18,400	17,600	16,500	13,800	7,800	4,700	3,200

In relation to these solubilities at various temperatures note that the melting points of the metals concerned in °C are Al: 658; Cr: 1830; Co: 1490; Cu: 1083; Fe: 1527; Mo: 2622; Ni: 1452; Pt: 1773; Ag: 960·5.

Note the very high value of *s* for titanium, which has led to the use of this metal in getter-ion pumps (§ 7.4); tantalum, thorium and zirconium are also used as getters (§ 6.13). These metals must be degassed at very high temperature (*see* Table 6.9) for a long time *in vacuo* to take full advantage of their marked absorption of hydrogen. The sorption is reversible. The electrical resistivity of the metal increases noticeably on hydrogen sorption and the metal becomes brittle.

Nitrogen. Insoluble in copper, silver and gold. Smithells (S17) reports that nitrogen is soluble in those metals capable of forming nitrides. The solubilities at various temperatures of nitrogen in iron are given in Table 6.4 and in molybdenum and tungsten in Table 6.5, both compiled from data given by Dushman (D1). The solubility varies as $p^{\frac{1}{2}}$, where *p* is the superincumbent nitrogen pressure. The values given should be regarded with reserve as the solubility depends on the metallurgical processing and pre-history of the metal, particularly in the case of iron. Moreover, various forms of the metal, *e.g.* wire, sheet, powder, chips, etc., will have different solubilities. Widely varying values have been given in the literature for the solubility of nitrogen in molybdenum; the figures given in Table 6.5 are probably minimum values.

Nitrogen is soluble in molten aluminium; at the melting point (658° C) *s* is

TABLE 6.4

Solubility s (in cm³/100 g) of nitrogen at 760 torr in iron

°C	750	890	900	1070	1300	1400	1420	1460	1540	1560
s	0·32	1·6	20	9·3	16·8	10·6	8·1	8·5	24·6	26·7

Note: α-phase up to 906° C; γ-phase from 906° to 1403° C and δ-phase from 1403° to 1537° C.

TABLE 6.5

Solubility s (in cm³/100 g) of nitrogen at 760 torr in molybdenum and tungsten

Metal	Temperature in °C			
	1200	1600	2000	2400
Molybdenum	0·84	3·44	8·4	16
Tungsten	0·001	0·015	0·088	0·304

TABLE 6.6

Solubility s (in cm³/100 g) of oxygen at 760 torr in copper

Temperature in °C	600	800	950	1000
s in cm³/100 g	5·0	6·6	7·0	10·9

TABLE 6.7

Solubility s (in cm³/100 g) of oxygen at 800 torr in solid silver

Temperature in °C	200	300	400	500	600	700	800
s in cm³/100 g	1·3	0·94	0·828[1]	0·905	1·26	1·84	3·37

[1] Note minimum value of s: alleged that, below 400° C, oxygen in silver in form of Ag_2O; above 400° C dissolved as oxygen atoms.

TABLE 6.8

Total amount of gas evolved by metals on heating in vacuum

Metal	cm³ of gas at S.T.P. per cm³ of metal
Aluminium	0·1 to 0·5
Copper	0·04 to 0·7
Iron	0·09 to 0·9
Nickel	0·4 to 40
Steel (1 % C)	150 to 200

about 1 cm³/100 g. Zirconium (*see* § 6.13) sorbs 1 atom of nitrogen to 11 atoms of zirconium when heated in nitrogen to form a solid solution of ZrN (report by Dushman, D1, of results by de Boer and Fast).

Oxygen. A considerable variation in results is given in the literature. Silver, copper and cobalt amongst the commoner metals sorb oxygen to give a true solution but other metals form oxides which are dissolved and it is difficult to distinguish true solution of the gas from that of the oxide (Dushman, D1).

Rhines and Mathewson (reported by Dushman, D1) give the values for the solubility of oxygen in solid copper given here in Table 6.6.

Steacie and Johnson (reported by Dushman, D1) give the values for the solubility of oxygen in solid silver given here in Table 6.7.

Smithells (S17) reports that the solubility of oxygen in iron is about 25 cm³/100 g over the temperature range from 800° to 1000° C, 147 cm³/100 g at the melting point (1535° C) and increases to 387 cm³/100 g at 1734° C.

6.4. The Degassing of Metals

To degas metals effectively they must be heated *in vacuo* to high temperatures. The gases evolved may come from adsorbed layers, dissolved gas, dissociation of chemical compounds of the gas with the metal, or from pockets of gas within microscopic interstices in the metal. Hydrogen, carbon monoxide, carbon dioxide, oxygen and nitrogen are commonly evolved gases on heating metals *in vacuo*, the rate at which a particular gas is released being largely dependent on the rate at which it diffuses through the metal.

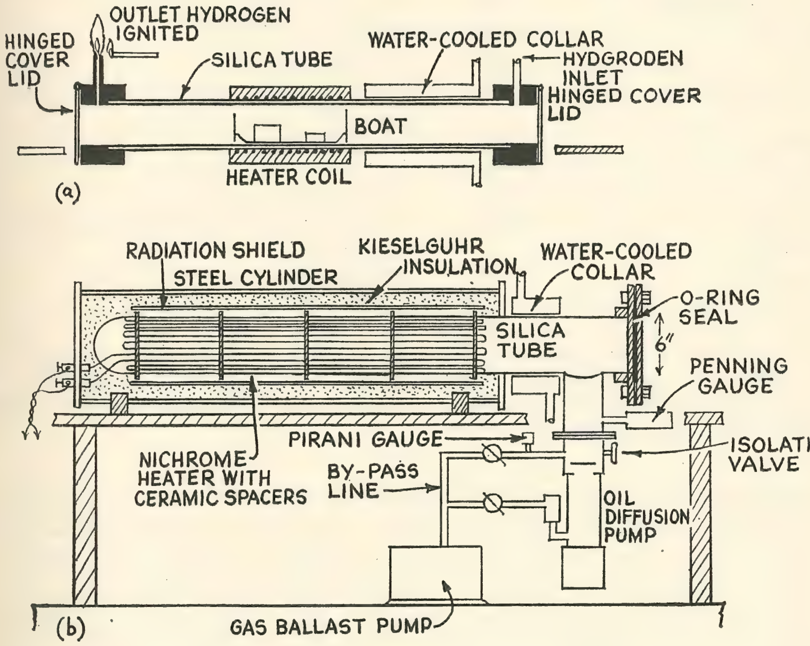

OUTLET HYDROGEN IGNITED
HINGED COVER LID
SILICA TUBE
WATER-COOLED COLLAR
HYDGRODEN INLET
HINGED COVER LID
BOAT
HEATER COIL
(a)
RADIATION SHIELD
STEEL CYLINDER
KIESELGUHR INSULATION
WATER-COOLED COLLAR
O-RING SEAL
SILICA TUBE
6″
PENNING GAUGE
PIRANI GAUGE
ISOLATION VALVE
NICHROME HEATER WITH CERAMIC SPACERS
BY-PASS LINE
OIL DIFFUSION PUMP
GAS BALLAST PUMP
(b)

FIG. 6.1

(*a*) A hydrogen stove for degassing metal parts
(*b*) A vacuum stove for degassing metal parts

Results given by various investigators vary widely as regards the total quantity of gas evolved, as this depends on the metallurgical processing and pretreatment of the metal concerned. Table 6.8 gives roughly the minimum and maximum amounts to be expected.

To degas metals they are heated in a vacuum stove or in a hydrogen stove (Figs. 6.1(*a*) and (*b*)). Though heating in a hydrogen atmosphere necessarily causes the metal to sorb this gas, it is re-evolved on baking *in vacuo* at 450° C. After stoving the metal it will normally only take up gas during storage as a result of adsorption; nevertheless, storage over long periods is preferably in a vacuum dessicator.

Metals to be used for electrodes of vacuum tubes (*e.g.* nickel, copper–nickel alloy, molybdenum, tantalum, iron, stainless steels) are degreased (subsequent to which they should only be handled by an operator wearing finger-stalls or gloves), and are then heated either in a hydrogen stove or a vacuum stove, the former being usually preferred as it is more convenient and ensures the removal of oxide films.

Maximum degassing temperatures are given in Table 6.9.

TABLE 6.9
Maximum temperatures for degassing metals and graphite

Metal	Temperature in °C	Gases evolved in order of decreasing amounts
Copper and alloys[1]	500	CO_2, CO, H_2O, N_2, H_2 (small %)
Graphite	1800	N_2, CO (at 2150° C)
Iron	1000	N_2, CO, CO_2, H_2
Molybdenum	950[2]	CO, H_2, N_2 (predominant at temp. $> 1200°$ C)
Nickel and alloys	950	CO, CO_2, H_2
Platinum	1000	
Steels	1000	CO, H_2, N_2, O_2, CO_2
Tantalum	1400	*See* § 6.13, should not be hydrogen-stoved
Titanium		*See* § 6.13
Tungsten	1800	Mostly CO; remainder CO_2, H_2
Zirconium		*See* § 6.13

[1] Copper alloys containing zinc (*e.g.* brass) cannot be heated in vacuum to more than about 200° C without volatilization of the zinc (vapour pressure is 10^{-5} torr at 211° C).

[2] Molybdenum may be heated to above this temperature (melting point is 2622° C) but it becomes brittle above 950° C.

Degreasing before hydrogen- or vacuum-stoving is satisfactorily done in a bath of trichlorethylene followed by a rinse in acetone and finally methyl alcohol. Drying is best arranged in a stream of dry air heated to 70° to 100° C.

After an electron tube has been evacuated and baked on the pumps, its electrodes are further degassed by induction-heating (Fig. 6.2(*a*)). If an induction heater is not available or inconvenient—as, for example, in the case of some large transmitting valves—heating of the electrodes by electron-bombardment is an alternative (Fig. 6.2(*b*)).

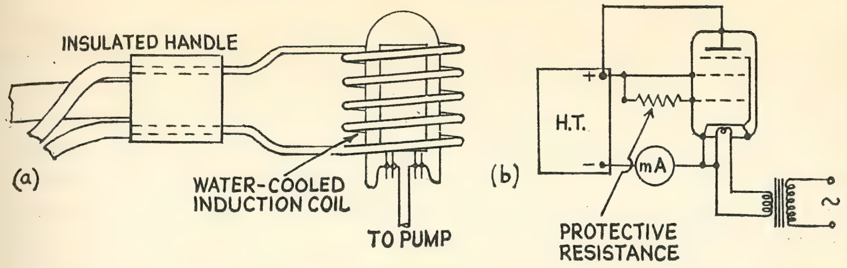


FIG. 6.2 Degassing of metal electrodes: (*a*) by induction heating; (*b*) by electron bombardment

6.5. Sorption and Desorption of Gas by Glass

When heated *in vacuo*, glass evolves considerable amounts of water vapour and, to a lesser extent, carbon dioxide and nitrogen, the quantities concerned depending on the nature of the glass, its treatment immediately prior to heating, and the temperature. The curves of total gas evolution against temperature for glasses heated *in vacuo* exhibit maxima; these occur at about 300° C for borosilicate glasses, 150° C for soda–lime glasses, and 175° C for lead glasses. On increasing the temperature beyond these optimum values, the gas evolution decreases at first but then rises steeply again at higher temperatures near and above the softening point of the glass. At temperatures up to 300° C, the adsorbed gases (chiefly H_2O and CO_2) are released; at higher temperatures around the softening point, decomposition of the glass causes much water vapour and moderate carbon dioxide evolution (from the carbonates of the glass mixture) and also other gases (including oxygen) depending on the glass composition. By previously annealing glass at high temperatures in air the subsequent gas evolution *in vacuo* is considerably decreased.

Sherwood (S18) gives data for various glasses indicating the total quantities of gas released by a dry glass surface at various temperatures. This data is briefly summarized in Table 6.10.

TABLE 6.10
Evolution of gas by a dry glass surface of area 350 sq cm in vacuum

Glass type	Total quantity of gas evolved in cubic mm at S.T.P.						
	100° C	150° C	200° C	300° C	400° C	500° C	600° C
Soda–lime	0	36	22	8	6	11	50
Lead	6	10	10	7	8	12	30
Borosilicate	4	20	20	10	16	12	30

To degas the glass envelope of a vacuum tube on the pump system the usual practice is to bake in an oven to a temperature about 50° C below the strain point of the glass. Maximum temperatures used are 400° C for lead glasses, 450° to 500° C for soda–lime glasses and 600° C for borosilicate glasses like Pyrex and Hysil.

A degassed, dry glass surface *in vacuo* will adsorb gas. However, the pressure within an evacuated glass tube invariably rises on sealing-off from the pumps, unless a getter film (§ 6.8) is present or ionic clean-up of gas takes place (§ 6.14). This pressure rise is due to gas evolved on heating the constriction in the exhaust stem tube on sealing-off and also due to subsequent slow evolution of gas from the glass, especially if it is heated. Nevertheless, it must be taken into account in some experimental work that gas admitted to an evacuated glass tube will be absorbed to some extent at the inner walls. For example, if dry air at a pressure of, say, 10^{-3} torr is expanded by a volume ratio of 100 into a pre-evacuated unbaked glass container, the pressure within the container (initially, say, 10^{-6} torr) will not be easily calculable from the ratio because of adsorption of the air by the glass. Water vapour and carbon dioxide are more readily adsorbed by glass than the permanent gases, especially by those glasses with a high alkali content.

6.6. Sorption and Desorption of Gases and Vapours by Rubbers, Plastics and Ceramics

Rubbers. Of the variety of natural and artificial rubbers on the market, the oil-resistant artificial rubbers Hycar OR, Neoprene and 'Buna N' or Perbunan (a German product) are the most widely used in vacuum technology and have similar properties from the point of view of vacuum seal-making, though Hycar probably outgasses at room temperature less than the others. These rubbers must not be exposed to temperatures in excess of 90° C; at temperatures up to 250° C, the silicone rubbers may be used but the difficulties encountered (§ 4.25) have led to a preference for metal gaskets (§ 4.27) where minimum outgassing is required and/or the temperature of the seal is to be raised above 90° C.

The considerable outgassing from Neoprene has already been considered in relation to its effect on the ultimate pressure produced by an oil diffusion pump (§ 2.14); this outgassing at room temperature may be reduced by degassing the Neoprene (or Hycar or Perbunan) gaskets by heating *in vacuo* to about 90° C before use.

Silicone rubbers evolve less gas than does Neoprene. Silastomers 50, 60, 70 and 80 (Midland Silicones Ltd.) are suitable for gasket fabrication.

Diels and Jaeckel (DJ1) give extensive tabulated data on the gas evolved by Perbunan, silicone rubbers and plastic materials (arranged after the scheme in the *Kunststofftaschenbuch von Saechtlieng-Zebrowski*, Hanser, Munich, 1954). This data is not precise (indeed, it could hardly be otherwise in view of the many variations possible in experimental procedure), but it does indicate the degree of outgassing from these materials *in vacuo*. Average approximate results given by Diels and Jaeckel for Perbunan are shown here in Table 6.11. Neither the type of pump system and its speed nor the vacuum gauge (probably a hot-cathode ionization gauge calibrated for nitrogen) are specified.

The values given by Diels and Jaeckel for the silicone rubbers vary widely but they do indicate considerably less outgassing than from Perbunan, and that the chief gases evolved are water vapour and carbon monoxide.

TABLE 6.11

Material (surface area 12 cm^2)	Pressure recorded in torr × 10^{-6} after pumping time of					Quantity of gas (in litre-torr × 10^{-3}) evolved in 1 hour
	10 min	30 min	1 hour	3 hour	5 hour	
Perbunan	190	125	90	53	41	108
Perbunan (previously heated)	35	12	6·0	2·3	1·7	28

Cloud and Philp (CP1) made comparative tests on the use of natural rubber as an O-ring gasket compared with lead. For rubber, the apparent vapour pressure recorded was 10^{-3} torr at 20° C. An equilibrium pressure of 10^{-5} torr was reached after pumping a rubber-sealed vessel of volume 0·5 litre by means of an oil diffusion pump of speed 25 litre per sec at the chamber and with a cold-trap filled with solid carbon dioxide. On using liquid air in this trap, the pressure fell to 5×10^{-6} torr. All pressures were recorded by a hot-cathode ionization gauge and were equivalent air pressures. For some of the gases and vapours evolved by natural rubber, the ionization probability is considerably greater than it is for air and, moreover, some of the more complex molecules concerned may decompose in the presence of the hot filament of the gauge, so these results are probably an over-estimate of the final pressures.

Plastics. An increasingly wide variety of plastic materials is being encountered in vacuum technology, but few of these are employed to any extent as constructional materials; the others are met with in the vacuum-drying (§ 11.4) of plastics and in the deposition of thin metallic films on plastics (*see* § 10.6, also Holland, H1).

Plasticizers such as camphor, triacetin, castor oil and dibutyl phthalate are frequently added to plastics to modify their flow and other properties at various temperatures. Some plasticizers (*e.g.* camphor and triacetin) have high vapour pressures in the free state; in general, their vapour pressures will be considerably lower in the bound state within the solid plastic, but they can still be troublesome. Holland (H1) recommends a diffusion pumping speed of 10 litre per sec for every litre of the chamber volume for equipment intended for the vacuum coating of metals on plastics and also stresses that the coating chamber and the pumping equipment need to be cleaned periodically to remove contamination due to plasticizer contamination (*see also* Chapter 10).

As a general rule it is best to exclude entirely plastic materials from vacuum systems, especially if pressures less than 10^{-3} torr are necessary, though notable exceptions may be made in the cases of polytetrafluoroethylene (P.T.F.E.; trade-names: Teflon, Fluon) which is a useful plastic for making demountable and rotatable seals (§ 4.26), and also Araldite, which is a valuable epoxy resin for making permanent, cemented seals (§ 4.14).

P.T.F.E. has a more extended working temperature range than any other plastic and superior resistance to chemical attack. Moreover, it has a very low coefficient of friction and is self-lubricating. These assets do, however, demand special precautions in making vacuum-tight seals (*see* § 4.26). The deformation temperature under load is 200° to 250° C, and the water absorption is negligible. Diels and Jaeckel (DJ1) report that a pressure of 2×10^{-5} torr is obtained after a pumping time of 20 min in a vacuum system in which a Teflon surface of 10 cm^2 area is exposed. Hogg and Duckworth (HD2), on the other hand, allege that Teflon has very little adverse effect at all on the exhaust time and that the reading of an ionization gauge (the system comprised a diffusion pump with a cold-trap filled with solid carbon dioxide) was the same after an exhaust time of 70 min, irrespective of whether the chamber was empty or contained exposed Teflon. According to Diels and Jaeckel, the chief gases desorbed by Teflon are nitrogen, carbon monoxide, oxygen, water vapour and carbon monoxide.

P.T.F.E. has excellent electrical insulation properties and low power factor; it is available as moulding powder, in the forms of film, rod, sheet and tape, and impregnated in metals, *e.g.* copper–fluon.

The use of polythene (polyethylene, Alkathene, *see* Glanvill (G14) for lists of trade names of plastics) tubing in vacuum systems at pressures greater than 10^{-3} torr, and particularly for backing-side tubulation is discussed in § 4.13, whilst isolation valves of this material are described in § 5.17. High-density polythene (Alkathene HD) has a higher softening point (approx 120° C as compared with 80° C), increased strength and rigidity. Hogg and Duckworth (HD2) report that, after 70 min pumping of a chamber by a diffusion pump with a cold-trap (filled with solid carbon dioxide) the pressure recorded by an ionization gauge with exposed polythene present is 20% greater than for a chamber free of this material. The chief gases evolved are nitrogen, water vapour, carbon monoxide, oxygen and carbon monoxide. The water adsorption of polythene sheet is 0·01% by weight in 24 hour.

Of other thermoplastic materials which might be used in special cases in the construction of vacuum plant, the following may be mentioned: polystyrene, polymethyl methacrylate (trade names are Perspex, Lucite, Plexiglass), polyvinyl chloride (P.V.C.), cellulose acetate and nylon. Of these plastics, only polystyrene has low outgassing in vacuum. Tabulated data for these materials, and several other plastics, on pump-down times, total gas evolution, surface resistance, water sorption, nature of gases evolved, and mass spectra of gases evolved, are given by Diels and Jaeckel (DJ1).

Ceramics. In general, very little outgassing occurs from the sintered ceramics (silicates and metal oxides) used for, *e.g.*, lead-in electrodes (§ 4.20), vacuum-tube electrode spacers, heater-cathode insulation in thermionic vacuum tubes, and as vacuum-tube envelopes (§ 4.11). Thus, a thermionic vacuum tube which has ceramic electrode spacers and is subjected to the usual bake-out, electrode degassing and getter-firing schedule adopted in processing, can readily have a residual total gas pressure after seal-off not greater than 10^{-7} torr, and, especially if barium getters are correctly used, (§ 6.10) may have a residual pressure as low as 10^{-9} torr.

The ceramics most frequently used in vacuum tube manufacture are mica, steatite and aluminium oxide. Mica occurs in nature in two forms: biotite and muscovite; the preferred form is muscovite [$H_2KAl_3(SiO_4)_3$], almost colourless silicate which cleaves readily into thin sheets and is widely used for electrode spacers and, in more specialized cases, for thin windows in Geiger–Müller tubes and ionization chambers. As compared with sintered ceramics, mica does give outgassing difficulties, since it contains 18% by weight of combined water and its surface can be normally regarded as saturated with gas. It is recommended to bake mica in air to 200° C to free it of water vapour before its use in a vacuum tube; baking up to about 600° C is possible (as when the tube is on the pumps during bake-out) but, above this temperature, separation into cleavage planes will occur, and the mica becomes silver-grey in appearance. By compressing the heated mica between flat surfaces, the cleavage planes can be recombined but the mica loses mechanical strength. Mycalex consists of mica with an inorganic binder.

Steatite, a natural magnesium silicate of high purity (talc or soapstone), has been much used for electrode spacers in place of mica, especially in ultra-high frequency thermionic vacuum tubes. It contains mechanically bound water which is driven off in the firing process necessary before use. It can be readily machined before firing, but, subsequently, is hard. During firing, a linear shrinkage of about 2% occurs at temperatures in excess of 870° C; firing must therefore be controlled carefully to prevent fracture. It is recommended (*The Tube Laboratory Manual, Massachusetts Institute of Technology*) that firing should be at a temperature between 1010° C and 1093° C where the rate of heating should not exceed 210° C/hour for thin sections and 150° C/hour for sections above ½ in. thick. Curing times at this temperature recommended are 15 min for ¼ in. sections and 45 min for ¾ in. and above. Furthermore, a subsequent stoving at 1000° C in a dry hydrogen atmosphere is desirable before use in a vacuum tube to be sealed from the pumps. Other magnesium silicates are Frequenta, Alsimag 243 and the various lavas (*e.g.* a range supplied by the American Lava Corporation). These all have a softening point of 1440° C and excellent electrical insulation properties combined with low power factor. Frequenta and Alsimag 243 are, however, superior in this last respect to steatite.

Aluminium oxide (alumina), Al_2O_3 (melting point 2050° C) is especially suitable, either in the tube form or sprayed on as a powder suspension in amyl acetate, for the insulation between the tungsten heater and the cathode in an indirectly-heated cathode. Steyskal (S9) points out that magnesium oxide (MgO), despite its higher melting point (2800° C), is not so suitable because it reacts chemically with tungsten and, moreover, evaporates in vacuum at 1600° C.

Porcelain (Sillimanite) is a very hard potassium aluminium silicate with excellent high voltage insulation properties and is used, in particular, for lead-in electrodes (§ 4.20).

Other ceramics used are beryllium oxide (BeO), zirconium oxide (ZrO_2), thorium oxide (ThO_2), titanium dioxides, and the recently-developed zircon porcelains and alkali-earth porcelains. Details of ceramics used for thermionic vacuum tube envelopes are given in § 4.11, and ceramic-glass seals are discussed in § 4.12. For further information on electrical properties, softening temperatures, sintering and processing *see* Steyskal (S9), *The Tube Laboratory Manual* (*Massachusetts Institute of Technology*), Diels and Jaeckel (DJ1) and manufacturers' data sheets.

Production of Low Pressures by Sorption

6.7. Absorption of Gases by Activated Charcoal

Before the advent of efficient vapour pumps the technique of producing a high vacuum by absorption of the gases on activated charcoal was frequently used. In modern vacuum practice, this method is only encountered in specialized applications, though Jepsen (J8) has recently devised systems comprising a small cold-cathode getter-ion pump (§ 7.7) with a fore-vacuum produced by charcoal at the temperature of liquid nitrogen, *i.e.* the mechanical backing pump is omitted.

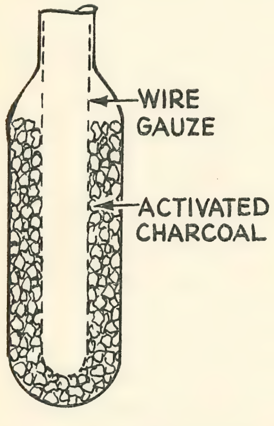


FIG. 6.3 A charcoal trap

Reimann (R3) states that the best charcoals are prepared from alder wood, box-wood, horn-beam, or the shells of various nuts or some fruit stones. Coconut shell charcoal is usually employed. Pieces of the wood or shell (not smaller than $\frac{1}{4}$ in. and with fine particles excluded) are destructively distilled at 500° to 700° C in an iron container until vapour evolution is no longer apparent. The charcoal produced contains tarry residues which are removed to increase the gas absorption efficiency by an 'activation' process, commonly by heating in steam at 800° to 1000° C for $\frac{1}{2}$ to 1 hour. The water in the activated charcoal is then driven off by heating the charcoal in a rough vacuum.

The activated charcoal is then placed in a borosilicate glass tube, preferably in the annular cylindrical gap between the walls of this tube and a central cylinder made of wire gauze to increase the exposed area of the charcoal (Fig. 6.3). This charcoal trap is then attached to the vacuum system, ensuring that a low impedance path is presented between it and the vessel. The vacuum system includes a rotary pump and also, in some cases, a vapour pump. The charcoal is then heated under vacuum to about 500° C, either within the bake-out oven, or an auxiliary oven, or by direct application of a gas-air flame. A Dewar flask containing liquid air (liquid nitrogen is preferred if there is any risk of contact with the charcoal since liquid air and charcoal may react explosively) is raised into position around the charcoal trap to reduce its temperature. Though the temperature of the charcoal will not drop to −183° C (the boiling point of oxygen) because of lack of intimate contact between the pieces of carbon, it is nevertheless possible to reduce the pressure in the system from, for example, 10^{-5} to 10^{-8} torr, or even lower, in this way. The pumping action is not fast, however, chiefly because it takes time for the charcoal to become thoroughly refrigerated; it may need an hour after the application of the liquid air for the lowest pressures to be attained. Espe (E5) has published the curves based on results given by Dushman (D1) and reproduced here in Fig. 6.4 for the decrease in pressure with time for the gases hydrogen, nitrogen and oxygen where the initial pressure is about 5×10^{-4} torr, and pumping is by degassed activated charcoal at −183° C.

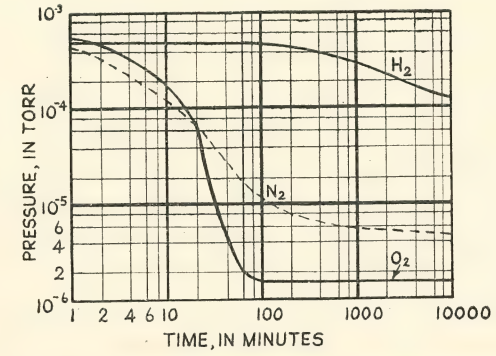


FIG. 6.4 Pressure against time curves obtained on pumping hydrogen, nitrogen or oxygen by means of a liquid-air cooled charcoal trap. Initial pressure: 5×10^{-4} torr

The charcoal can be freed of absorbed gases by re-heating *in vacuo*; indeed the same charcoal trap may be re-used repeatedly.

Activated charcoal absorbs gas readily not only because of the large surface area it presents (adsorption) but also, and chiefly, because gas is taken up within the porous structure of atomic dimensions (absorption). In the case of some gases, chemisorption occurs and this may result in the gas re-evolved on heating being different from the gas originally absorbed, *e.g.* absorbed oxygen is desorbed as carbon monoxide. The volume of gas at a given pressure which is absorbed under given conditions by unit mass of activated charcoal of a given kind varies greatly with the nature of the gas. In general, the quantity of gas absorbed is greater, the higher its boiling point at atmospheric pressure. Espe (E5) gives figures based on Dushman (D1) and reproduced here as Table 6.12.

Chabasite, a calcium aluminium silicate, and the similar material 'molecular sieve', no. 5A (*British Drug Houses Ltd.*), are materials with an average pore diameter of about 5×10^{-8} cm. Within a glass finger surrounded by liquid air these materials, after a preliminary bake at 100° C, act as extremely effective pumps and are much more convenient and effective than charcoal. A new technique in vacuum promises to develop from their application.

TABLE 6.12
Absorption of various gases by charcoal

Gas	Temperature of charcoal, °C	Prevailing gas pressure, torr	Quantity of gas absorbed in cc at N.T.P. per gram of charcoal
He	−190	705	1·84
H_2	0	744	1·55
	−183	760	100 approx
N_2	0	774	13
	−183	760	185
A	−183	760	205
CO_2	0	755	66
	−78	760	160
O_2	−183	760	250

6.8. Getters: classification

The most widely-practised method of producing low gas pressures by sorption is by the use of getters. It is useful to classify getters into three main groups (Espe, Knoll and Wilder, EKW1):

(*a*) **Flash getters** which are chemically active, electropositive, volatile metals which are evaporated by heating (induction heating or by electric current through a supporting metal spiral or tube) in the residual gases within a container, *e.g.* a radio receiver valve, which has been previously evacuated by conventional methods, *e.g.* a combination of rotary and vapour pumps.

Ehrke and Slack (ES1) distinguish in this case between the process of **dispersal gettering** in which gas is taken up whilst the getter is being volatilized, and **contact gettering** in which the film of getter material deposited by the volatilization on the container walls or other solid surface will continue to take up gas. In dispersal gettering, the metal in its vapour state presents its maximum possible 'surface' to the gas; in contact gettering, adsorption is followed often by diffusion into the inner layers of the metal film.

The other two main groups of getters are of the contact type:

(*b*) **Bulk getters** which are selected metals in sheet or wire form which are heated so that they sorb gas;

(*c*) **Coating getters** consisting usually of non-volatile metal powders which are sintered on the surfaces of electrodes in special types of vacuum tube which are maintained continuously at temperatures in the range 200° to 1200° C during service.

6.9. Flash Getters

The chief application of flash getters is in the final stages of the evacuation of electron tubes, *e.g.* radio receiver valves, transmitter valves, rectifier valves and cathode-ray tubes. Some types of gas-discharge tube are also concerned. A more specialized use is in the recently developed getter-ion pumps (§ 7.4).

In the processing of an electron tube, the procedure is, in brief, evacuation by a rotary/diffusion pump combination (for small radio-receiver valves in mass production, some manufacturers use a rotary pump alone), bake at 400° to 550° C, cathode heating, induction heating of electrodes, firing of getter, seal-off. In some cases, the last two stages are reversed, *i.e.* seal-off precedes firing of the getter. In the selection of the getter the following factors are concerned:

(*i*) It must not be adversely affected during storage prior to use.

(*ii*) The act of sealing-in of the electrode assembly within the tube envelope must not affect the getter.

(*iii*) During the bake, the getter must not have appreciable vapour pressure ($< 10^{-4}$ torr) at the temperature attained.

(*iv*) On firing the getter, the heat applied should be localized within the area of the getter itself, the dispersal should take place rapidly, gas should not be released by the getter or its support, the inner wall of the container on which the getter film is deposited should not be too hot, the volatilized metal must not spread to insulators in the electrode assembly, and clean-up of the residual gases should be as effective as possible.

(*v*) The getter should continue to sorb gas after the tube has been processed.

(*iv*) The vapour pressure of the getter material and its reaction products with the residual gases in the tube should be negligible at the tube operating pressure.

In connection with (*iv*) the nature of the residual gases is important. In non-baked vacuum vessels of glass or metal which have been exhausted by oil diffusion pumps, the residual gases are primarily water vapour, hydrocarbons and hydrogen; if a mercury diffusion pump is used, mercury is also present unless effective refrigerated traps are used (§ 2.11). It is not possible to be dogmatic about the residual gases in a baked electron tube, as much depends on the processing schedule adopted, on the electrode materials used, on the type of glass or other material from which the tube envelope is constructed, and on the methods adopted for degassing the electrodes prior to assembly (*e.g.* hydrogen-stoving or vacuum-stoving, the former being commoner, § 6.4). Wagener (W6) alleges, however, that there is reasonable agreement about the main constituents of the residual gas in thermionic vacuum tubes; they are:

Oxygen. The presence of this gas is particularly deleterious to activated oxide-coated thermionic cathodes. It is likely to arise on the dissociation of oxide layers on electrode surfaces. However, such oxide layers are largely removed by hydrogen-stoving and, moreover, even at 1000° C, the dissociation pressures of the oxides of the metals commonly used (*e.g.* Ni, Mo, W) are only of the order of 10^{-10} torr.

Carbon monoxide. Evolves continuously from nickel components due to carbon diffusing from the interior of the metal and reacting with oxygen at the surface. Carbon monoxide is one of the chief gases present whereas any free oxygen is likely to be used up in reaction with carbon.

Carbon dioxide. Originates from oxide-coated cathodes since this oxide is normally produced by dissociation of barium and strontium carbonates. The carbon dioxide will normally react with other electrodes to produce surface carbonate layers, which then dissociate to produce carbon dioxide again. This dissociation of carbonate layers is much more vigorous than that of oxygen layers.

Nitrogen. Evolved by molybdenum components.

Hydrogen. Not only is hydrogen widely used in the metallurgical processing of the metals used for valve components, it is also employed in the preliminary cleaning of electrodes by hydrogen-stoving.

Water vapour. Glass and mica evolve water vapour.

Hydrocarbons. These are frequently observed in mass spectrometric studies of residual gases in vacuum tubes; acetylene is often noted.

Of these gases, it is most important to eliminate as far as possible those which adversely affect thermionic cathode emission. They are oxygen, carbon monoxide and carbon dioxide; as oxygen is probably largely converted to carbon monoxide, it appears that the carbon oxides are the most important gases from the gettering point of view (Wagener).

If the curves of vapour pressure against temperature for the metals are studied (Fig. 14.21) in relation to the requirements that the vapour pressure of the getter should not exceed about 10^{-6} torr at bake-out temperatures of 400° C, and yet should reach a significant value of about 1 torr at a reasonably attainable firing temperature of about 800° to 900° C to ensure quick dispersal, it is seen that barium is suitable. Fortunately, this alkali-earth metal also absorbs strongly by both dispersal and contact gettering the gases which it is required to handle in residual vacua; in the form of the pure metal (with suitable protection against atmospheric action before use) and in special getter alloys and preparations, it is therefore the most used getter.

Other metals have, however, been employed as flash getters, but some of them have now virtually become obsolete. However, these are considered briefly first.

Phosphorus is used as a getter particularly in the electric lamp industry for the production of both vacuum- and gas-filled bulbs because it gives rise to a deposit on the glass envelope which is transparent to light and is inexpensive (Reimann, R3; Dushman, D1). *Aluminium* is not used as an electron-tube getter; however, it is much used in vacuum coating technology (Chapter 10) and has been used in the form of a coating getter as aluminium-plated iron for the oxygen released slowly from combination with the carbon content of iron electrodes. Some dispersal gettering of oxygen, carbon dioxide, water vapour and nitrogen takes place, but only oxygen is contact-gettered by a freshly deposited aluminium film. *Calcium* is not as effective as magnesium, but it has been used in the past to a limited extent because the deposited film is non-conductive. *Magnesium* was much used for gettering electron tubes in the period 1920 to 1930. The ribbon surface is first scraped free of corrosion and is then clipped or spot-welded on to a nickel disc. This disc (usually about 1·5 cm dia) is welded via a support rod on to a suitable metal part within the vacuum-tube envelope, *e.g.* on a pinch wire, and is induction-heated to about 800° C to volatilize the magnesium quickly. Alternatively, the cleaned magnesium ribbon may be placed within a tungsten spiral which is heated by the passage of electric current. According to Reimann (R3) oxygen is rapidly gettered by magnesium both on dispersal and by contact. Carbon monoxide is also dispersal-gettered but contact gettering of this gas is slight. Carbon dioxide undergoes reduction to the monoxide which is dispersal-gettered fairly rapidly but only slightly absorbed by contact gettering. Nitrogen is absorbed but is re-liberated, even at room temperature. Hydrogen is only slowly gettered, unless in the atomic form; water vapour undergoes chemical reaction to give hydrogen.

6.10. Barium and Barium Alloys and Preparations as Getters

Barium getters: oxygen, carbon monoxide, carbon dioxide, hydrogen, nitrogen and water vapour. Indeed, all but the inert gases and possibly some complex organic molecules are sorbed during dispersal and retained within the film deposited, which, furthermore, contact-getters. As barium is very active it must be protected against atmospheric action during storage and within the vacuum tube prior to firing. As a getter, it is available in the following forms:

(*a*) Copper, nickel or iron clad pellets. A tube of one of these metals is filled with liquid barium under vacuum during manufacture (*Kemet Laboratories Incorporated*). The tube is then drawn down to size and cut into small, cushion-shaped pellets. Though the barium is then substantially protected from the atmosphere, some air leakage is likely, especially through the cut-off ends of the pellet. It is therefore necessary to store the pellets in a well-stoppered bottle (preferably with the stopper paraffin-waxed) or, better, in a vacuum desiccator, or evacuated or inert gas-filled glass bulb or tube. In use, a pellet is often mounted on a nickel disc in the vacuum tube; to hold this pellet in place, a cover disc with suitable openings or a wire gauze is welded over the pellet (Fig. 6.5(*a*) and (*b*)). This arrangement is induction-heated by means of an eddy-current heater coil outside the tube and with its axis usually perpendicular to the plane of the getter mount. To degas the getter mount before firing, its temperature may be raised to 750° C; subsequent heating to 850° or more causes the barium to reach such a high vapour pressure (1 torr at 858° C) that it bursts through the ends of the pellet.

A more favoured arrangement of barium getter is that shown in Fig. 6.5(*c*). Originally introduced by the Kemet Laboratories Incorporated and known as KIC (Kemet iron-clad) wire, it consists of a barium (or barium alloy) filled iron tube of external diameter about 0·02 in. with one side ground flat so that the thickness of the iron covering there is reduced to about 0·003 in. This wire may be induction-heated or heated by the direct passage of electric current. In the former case, it is usually mounted across a simple nickel or iron-wire frame to make a closed loop; in the latter case, the KIC wire may be connected across two of the pinch wires of the electron tube; if these wires are normally used for connection to electrodes, the KIC wire may be heated to above the firing temperature, after the getter deposit is formed, to burn out the temporary connection made. One cm of 0·02 in. dia barium-filled KIC wire yields on the average 2·5 mg of barium.

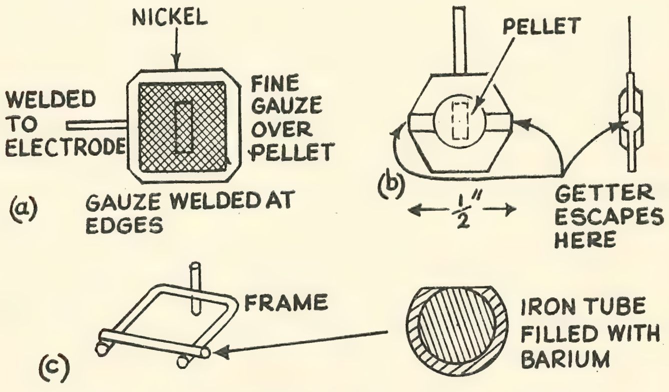


FIG. 6.5 Getter mounts

(*b*) To reduce the possibility of atmospheric action during storage and during the heating in air on sealing the mounted electrode system into the envelope of the electron tube, and in cases where the getter is mounted in the tube in positions exposed to heat (*e.g.* in miniature tubes and in some types of hard glass transmitting valves) it has become usual practice to alloy the barium with magnesium and/or aluminium. Typical of such alloy getters are those of the 'Stabil' type manufactured by the Società Apparecchi Elettrici e Scientifici, Milan (SAES), which consist of a barium-aluminium alloy either in a straight, grooved iron tube which is welded to a nickel or iron alloy wire bridge (Fig. 6.6(*a*) and (*b*)) or within a groove in a ring of stainless steel (Fig. 6.6(*c*)). Non-magnetic getters are also available, particularly for use in cathode-ray tubes. The barium alloy used is stable up to temperatures of 600° C; it is therefore not necessary to protect the exposed surface of the alloy within the groove of the getter mount. Indeed, these getters can be exposed to air for long periods (though this is undesirable practice) and can be washed in distilled, or preferably de-ionized, water and subsequently in alcohol without special precautions. A wide range of sizes is available extending from getters intended for very small hearing-aid valves to those for cathode-ray tubes and large power amplifier and transmitter valves. A disadvantage of the stable barium–aluminium alloy is that it must be heated to about 1100° C for effective dispersal, a temperature at which the getter support may vaporize slowly. However, their small thermal capacity and convenient loop shape ensure effective heating with small power dissipation, so that performance is very satisfactory provided due attention is paid to correct mounting of the getter and control of the induction heating.

(*c*) A tantalum wire spiral is coated with a mixture of barium and strontium carbonates (as used for oxide-coated thermionic cathodes). On heating *in vacuo* to about 850° C, the carbonates dissociate to oxides; further increase of the temperature to 1300° C produces free barium and strontium due to the reducing action of the tantalum. This type of getter is known as **Batalum**. A disadvantage is that the tantalum oxide formed dissociates very slowly and increases the pressure in a sealed-off tube. The replacement of the carbonate mixture by barium berylliate ($BaBeO_2$) is a subsequent development which avoids the evolution of carbon dioxide.

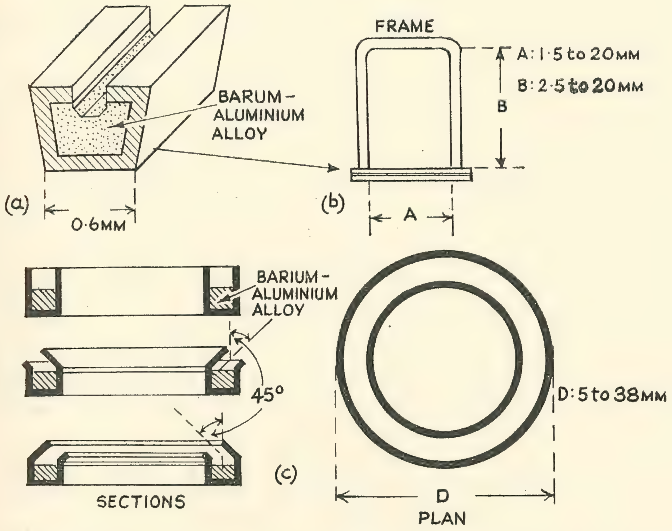


FIG. 6.6 Modern barium alloy getters (*Courtesy of Società Apparecchi Elettrici e Scientifici, Milan*)

Two other types of these so-called 'reaction getters' are the **Alba** getter, in which barium oxide is reduced in the presence of aluminium to give free barium, and the **Bato** getter, in which barium is evaporated from a mixture of barium–aluminium alloy, iron oxide and thorium powder. This mixture is made available as a nickel-covered pellet.

6.11. Contact Gettering by Barium Films

The pumping speed, S_G, of a film of getter of surface area A can be calculated by introducing a *sticking factor*, α, defined as the ratio of the number of molecules retained by the film to the number incident per unit time. The number of molecules, N, retained per second is therefore given by:

$$N = \tfrac{1}{4}\alpha n \bar{v} A = \alpha n \sqrt{\frac{RT}{2\pi M}}\, A \qquad (6.5)$$

where n is the number of molecules of the gas per cc, $\bar{v}$ is the mean velocity of the molecules at an absolute temperature T, M is the molecular weight of the gas and **R** is the gas constant (*see* Appendix A). If V is the volume of the enclosure, then $\frac{dp}{dt}$, the rate of reduction of the pressure at time t, is given by:

$$\frac{dp}{dt} = -\frac{S_G}{V}(p - p_u)$$

where p_u is the ultimate pressure obtained. Neglecting p_u (compared with p) and considering that $p = n\mathbf{k}T$, the speed, S_G, can be expressed by:

$$S_G = \left(-V\frac{dn}{dt}\right)\Big/ n \tag{6.6}$$

But $N = V\frac{dn}{dt}$, hence substitution from equation (6.5) in equation (6.6) gives:

$$S_G = \alpha\sqrt{\frac{\mathbf{R}T}{2\pi M}}\,A \tag{6.7}$$

Substituting $\mathbf{R} = 8{\cdot}314 \times 10^7$ erg deg^{-1} mol^{-1} and $T = 300°$ K (27° C),

$$S_G = \frac{63\alpha A}{\sqrt{M}}\ \text{litre/sec}^{-1} \tag{6.8}$$

To use this result, the values of α for the various gases for the type of getter film in question must be known. By comparing the maximum theoretical speed ($\alpha = 1$) with the gettering rates for barium given by Wagener (W6), Alpert (A9) gives values for the various gases shown in Table 6.13.

TABLE 6.13
Sticking factors, α, for a freshly deposited barium film at room temperature

Gas	CO	CO_2	O_2	H_2	N_2
α	0·4	0·6	0·02	0·001	0·003

These figures are suspect, however, first, because in practice a mixture of gases is almost always concerned and the value of α for a particular gas will depend markedly on gas already sorbed; second, because considerable variation with evaporation conditions will be experienced, and, thirdly, the rate of gettering falls off markedly, especially for the apparently favoured carbon oxides. Accepting these values, nevertheless, the initial speed of gettering for carbon monoxide will be given by equation (6.8) as

$$S_G = \frac{63 \times 0{\cdot}4}{\sqrt{28}} = 4{\cdot}75\ \text{litre/sec}^{-1}\ \text{cm}^{-2}$$

For oxygen, the initial speed would be 20 times smaller, in accordance with the values for α given in Table 6. For the mixture of gases in a residual vacuum at low pressure ($< 10^{-3}$ torr) it can be considered, therefore, that a fresh barium deposit of, say, 10 cm^2 in area will provide an initial pumping speed of a few litre per sec.

This speed will, however, fall off with time. Wagener (W6) shows that there are two types of decay: for oxygen, water vapour and hydrogen, the gettering rate for barium (produced from KIC wire) for a constant manifold pressure (4×10^{-4} torr in his experiments) remains nearly constant at first and then decreases slowly within a period of half to one hour; on the other hand, for carbon monoxide, carbon dioxide and nitrogen, the gettering rate falls off right from the beginning, *e.g.* for carbon monoxide it falls to practically zero (from an initial value of 2 l/s in the experiment) in about 5 min. It was also observed that the long-term fall-off gave rise to a pronounced change of the bright barium film to a deposit of milky appearance, probably an oxide, hydroxide or hydride, whereas the visible appearance of the barium film remained unchanged during the short term decay observed with carbon monoxide. Wagener suggests from considerable experimental evidence that the reaction between the barium and carbon monoxide or dioxide or nitrogen produces a protective surface layer on the barium in the first few minutes of gettering which inhibits further gas absorption. Moreover, once the barium film getter action was inhibited by carbon monoxide take-up, it could not then absorb another gas, *e.g.* oxygen. This result is of considerable practical significance in gettering electron tubes in which carbon monoxide is a likely constituent of the residual gaseous atmosphere. A single grid of a small radio receiver valve may evolve sufficient carbon monoxide to reduce the gettering rate in this way unless the component is adequately degassed either prior to assembly or on the pump before flashing the getter.

Wagener also shows that, if the getter flash temperature is increased, the resultant getter deposit is more porous and hence more effective. For example, if the KIC wire is heated at 880° C for 3 min the gettering rate for carbon monoxide falls to practically zero within 5 min, but if the temperature is 1350° C for 9 min, the decay time is about 15 min. Furthermore, if the deposited getter film temperature is increased from 60° to 160° C, the decay time for carbon monoxide is increased from 5 min to 15 min for a flash temperature of 880° C, but the initial gettering rate is not affected, the conclusion being that the increase of the film temperature increases diffusion of the gas into the layer. If a barium film which has become saturated with carbon monoxide at 60° is then heated to 300° C, the total desorbed quantity of gas is less than 1/1000 of the total gas sorption, indicating that the gas has entered into chemical combination with the barium, *i.e.* the process is chemisorption. This heating of the barium film does, however, partially restore its gettering action, presumably because the sorbed gas diffuses into the film interior and so reduces the protective surface layer.

Reimann (R3) and Wagener (W7) have alleged that the gettering action at low pressures is enhanced considerably by the impact of electrons on the gas molecules to produce atoms, metastable molecules and ions. This contention has apparently been disproved by the subsequent experiments of Wagener (W8) and Bloomer (B24). The latter author also shows that, when the getter rate of a barium film begins to fall, oxygen is still taken up if it first comes into contact with a nearby incandescent filament. It is often the practice in the radio valve manufacturing industry to flash the getter in the presence of ionized gas (especially where a rotary pump only is used so that the residual pressure is about 10^{-3} torr initially and the gas becomes ionized in the r.f. field produced by the induction heater), and many workers probably still believe that the presence of the discharge enhances the gettering action. It might be said that this question as to whether the presence of excited and ionized gas atoms and molecules increases gettering speed is not fully answered in the many circumstances which may prevail depending on the nature of the residual gases.

A further interesting result given by Bloomer (B24) is that a barium film freshly deposited in a very good vacuum (10^{-7} torr) does not immediately take up admitted oxygen; indeed the pumping action of the getter does not begin for about 15 min after oxygen is admitted. In a later paper, Bloomer (B25) concludes that the 'variation with temperature of the amount of molecular oxygen taken up by barium films is explained by Mott's theory of oxidation'. Furthermore, if the barium film temperature is below 40° C, the surface oxide film grows to about 50 Å in thickness and acts as a barrier, but at higher temperatures, the film oxidizes through its whole thickness. Subsequently, Bloomer (B26) studied also the uptake of carbon monoxide by barium getters and alleges that this gas is dissociated at the barium film surface to produce an oxide layer containing free carbon. For a film temperature below 80° C, the surface layer grows to only about 50 Å in thickness when it becomes protective, but above 80° C, the whole of the barium film is used up in reacting with absorbed carbon monoxide. About 1 in 80 of carbon monoxide molecules incident on the barium film surface in a given time are absorbed at 20° C and about 1 in 40 at a film temperature of 170° C.

Ehrke and Slack (ES1) have determined experimentally the capacities of various getters at 27° C for various gases. Their results are shown for barium in Table 6.14 with magnesium given for comparison.

TABLE 6.14

Capacities of barium and magnesium films at 27° C as getters

Getter	Amount of gas measured in litres at a pressure of 10^{-3} torr taken up in saturating 1 mg of the getter			
	Oxygen	Carbon monoxide	Carbon dioxide	Nitrogen
Barium	15·2	—	87·5	9·5
Magnesium	20	—	0	0

In view of the findings of Wagener and Bloomer recorded above, it is not surprising that no figure is given for carbon monoxide. If the getter deposit is not a bright mirror-like film but has a diffuse porous structure, the contact gettering capacity is considerably increased. Thus, Ehrke and Slack produced diffuse deposits by evaporating the getter in an inert gas atmosphere at a pressure of 1 to 3 torr, pumped away this gas, and then found that the capacity of magnesium for oxygen was increased 10 times; of barium for oxygen, 3 times; for nitrogen, 4 times and for carbon dioxide, 11 times. Reimann (R3) has also established that the brown to black porous barium film obtained on flashing the getter in a moderate vacuum (say, 10^{-3} torr as produced by a mechanical rotary pump in receiver valve manufacture) has a much greater contact gettering capacity than the bright metallic film produced by evaporation in a high vacuum (say, 10^{-6} torr).

P. della Porta (P7) stresses that the working temperatures in some types of valve reaches almost 200° C and that it is therefore important to consider the contact gettering capacity of barium films at these higher temperatures. Table 6.15 based on his results shows the total absorption capacity at various temperatures of bright barium mirrors produced by evaporating 1 mg of getter at a residual gas pressure of 10^{-4} torr to produce a deposit of area 10 sq cm. The temperatures recorded were attained by switching on a heater after the getter was fired.

TABLE 6.15

Total absorption capacity of bright barium mirrors

Gas	Quantity of gas absorbed measured in litres at a pressure of 10^{-3} torr per mg of barium; deposited film area: 10 sq cm				
	20° C	100° C	200° C	300° C	400° C
Oxygen	50			57	
Water vapour	35			72	
Hydrogen	45	50	55	90	100
Carbon dioxide	6·0	20	33	58	66
Carbon monoxide	7·2	40	44	90	100
Nitrogen	3·3	4·8	34	50	51
Dry air	6·4	16·0	46	56	56

These figures for 20° C are higher than those recorded by Ehrke and Slack at 27° C except in the cases of hydrogen and nitrogen (*cf.* Tables 6.14 and 6.15), no doubt due to the difference in experimental conditions, method of measurement and probably the deposit area. Also, della Porta evaporated the barium from a 50–50 barium–aluminium alloy, but in a manner where the evaporation of aluminium was negligible. It is noteworthy also that della Porta gives a figure of 7·2 l.µ/mg for carbon monoxide (an important residual gas in electron tubes, § 6.9) whereas Ehrke and Slack do not record a figure for this gas, nor do they consider water vapour.

The important conclusions reported by della Porta in connection with barium getters may be summarized as follows:

(*i*) At increased temperatures, the barium film absorbs greater quantities of gas approaching the amounts required for formation of a chemical compound between the barium and the gas concerned.

(*ii*) High operational temperature of the valve envelope on which the barium film is deposited prevents the formation on this film of surface barrier layers and so reduces greatly the poisoning effect on thermionic cathodes observed with certain gases (notably oxygen and carbon monoxide) at room temperature.

(*iii*) It is preferable to evaporate barium getters on to cold surfaces rather than hot ones (though the film temperature may be raised during subsequent operation of the valve) because deposition on a hot surface seems to result in the formation of large crystals in the film with consequent decreased absorption capacity.

(*iv*) Operational temperatures up to 400° C do not cause gas evolution from the barium film.

(*v*) It is possible to restore the vacuum within a valve by heat treatment of barium getter deposits at temperatures of 200° to 250° C, and, furthermore, exhausted barium deposits can be at least partially regenerated by heating the film to 350° C for a certain time.

6.12. Choice and Use of Flash Getters

It is not a straightforward matter to specify the type of flash getter suitable for a particular purpose. The selection depends on a number of factors: the metal parts within the tube and how they were degreased and degassed prior to assembly; whether the envelope is glass or metal, and what type of glass or metal; how the sealing-in of the electrode system within the envelope is accomplished in relation to temperatures attained in the region of the mounted getter; the pumping schedule adopted, including the time of bake-out and induction heating; the type of pumping system, *e.g.* whether it is a large automatic mass production plant or a small laboratory system, and whether the pumps are mechanical and/or diffusion types and the kind of pumping fluid used. It is hence necessary to arrive at the best choice of getter by experimental trial. Nevertheless, some guiding hints can be given (*see also* Table 6.16).

For low power valves and miniature tubes, barium getters are used. Barium alloy getters of the KIC and of the SAES types (§ 6.10) are generally preferred as they are readily flashed, evolve a minimum of gas, and a preliminary degassing without volatilization is easily arranged in the pumping schedule. Moreover, having very small thermal capacity, they do not undesirably heat up the adjacent envelope wall on which the getter film is to deposit (which may cause peeling of the deposit, especially if the getter-wall clearance is small). Moreover, within metal envelope tubes where induction-heating is not possible, they can be readily heated by the direct passage of electric current.

Though they will yield less barium for a given weight of getter, the barium–magnesium and barium–aluminium alloys are usually preferred to the pure barium type. They are also produced in the KIC wire form with the consequent advantages just mentioned. The alloy has the advantage that it is more resistant to atmospheric action and especially to heating during the sealing-in of the electrode assembly into the valve envelope. Moreover, though magnesium is not such an effective overall getter as barium, it does contact-getter oxygen with greater efficiency than does barium. If particular insurance against spoilation of the getter during seal-in is desired, a barium–aluminium alloy getter is chosen: the aluminium has practically no direct action as a gas absorber; its chief function is to stabilize the getter during manufacture, storage and any rise of temperature during sealing-in.

The actual weight of getter material used should be such that pre-heating to degas the getter and its support, final firing during pumping and firing after seal-off are all possible. Volatilization of the getter after seal-off (modern electron tube manufacturing methods provide for the tube to be sealed-off before the getter is evaporated) is important because evaporation of the getter results in a rapid reduction of the pressure in the tube to below that attained by the pump system (Bailleuil-Langlais, B27). A residual pressure of 10^{-3} torr may be reduced quickly to 10^{-6} or even 10^{-7} torr on effective gettering and in the subsequent ageing of the tube the pressure may decrease to as low as 10^{-9} torr.

Getter supports should not be exposed to air for long periods before use or allowed to collect dirt or grease; moreover, during assembly the operator should wear protective finger-stalls. Pre-firing to degas barium getters is best at 600° to 700° C and the volatilization temperature should be 900° to 1300° C. Though rapid evaporation is desirable, too high a firing temperature may produce such high vapour pressure that the getter diffuses undesirably over the tube; in extreme cases, the rapid release of latent heat of condensation may crack the glass wall on which the getter is deposited. Evaporated barium may reach the surface of an oxide-coated cathode but this does not matter as it enhances rather than inhibits the electron emission. Barium getters cannot be used in the presence of mercury; a bulk getter such as zirconium (§ 6.13) may be used in mercury vapour discharge tubes.

Barium and barium alloy getters in the form of pellets mounted on nickel or iron-alloy flags, or preferably in the KIC wire or 'Stabil' ring form, are used in sub-miniature, miniature, low power and medium power radio valves and also in cathode-ray tubes, photocells and gas-filled tubes.

The Batalum getter (§ 6.10) should be degassed at a temperature of 800° to 1100° C and fired at 1200° to 1300° C. It is used in small radio receiver valves and other tubes with oxide-coated cathodes. Of the reaction getters (§ 6.10) the Bato type is the more popular; it is fired at a temperature of 800° to 900° C and is used in medium and high power radio valves.

6.13. Bulk and Coating Getters; Sorption of Gas by Heated Filaments

The following refractory metals absorb appreciable quantities of gas when heated to temperatures at which their vapour pressures are negligible: tantalum, colombium, zirconium, titanium, thorium, tungsten and molybdenum (*see also* § 6.3). These metals can consequently be used as getters of a specialized kind; moreover, it is important to study their sorption and desorption actions when heated in other connections. They are available in the forms of wire, foil, strip and rod, or, alternatively, as a powder. Heating is therefore conveniently arranged by the direct passage of electric current except in the case of powder which must be on a suitable support.

Tantalum (melting point 2850° C). Pirani (P8) found that tantalum wire when heated to temperatures approaching 800° C sorbed about 740 times its own volume (at S.T.P.) of hydrogen and that this gas take-up increased noticeably the electrical resistivity of the metal and also rendered it brittle. Subsequent heating in vacuum caused three-quarters of the gas to be re-evolved, the remaining gas being released only if the tantalum were melted. The indication is therefore that the occluded hydrogen is in solution in the metal. Subsequent work by Sieverts and Bergner (SB2) showed that the rate of absorption increased with temperatures in the range from 500° to 1200° C but that the total amount of gas absorbed decreased with temperature rise (*see* Table 6.3). Fetkenheuer and Cremer (FC1) give the optimum temperature for hydrogen absorption as 600° C. Wright (W9) has shown that the gas take-up depends markedly on the cleanliness of the surface, so the tantalum should be initially degassed, particularly to rid it of oxide skin, by heating it in vacuum to 2000° C.

Heated tantalum also sorbs oxygen, nitrogen and carbon monoxide. Oxygen is sorbed readily at 750° C and rapidly at 1500° C up to a maximum volume of gas at S.T.P. equal to about 20 times the volume of the tantalum. Above 1500° C, Ta_2O is formed, corresponding to an oxygen volume at S.T.P. of 2500 times the volume of the metal. At above 2000° C, the dissolved (but not the chemically combined) oxygen is re-evolved. Nitrogen is sorbed slowly at temperatures below 1300° C, but at 1750° C the volume of nitrogen at S.T.P. can reach a maximum of 80 times the volume of the tantalum. Water vapour and hydrocarbon dissociate in the presence of heated tantalum (*cf.* tungsten).

Tantalum is used as a getter for medium and high power valves, especially transmitting valves having a molybdenum or tungsten anode which runs hot in service. Either a thin strip of tantalum is welded on to the electrode or the powder is sintered on. For example, an appropriate part of the surface of a molybdenum anode is first roughened, the tantalum powder in a suitable binder is painted on, and the subsequent application of heat during processing of the valve sinters in the tantalum and drives off the binder material which is pumped away (Reimann, R3). A controllable supply of hydrogen can be obtained by heating a tantalum wire in the gas.

Columbium (niobium) (melting point 1478° C) is similar in its behaviour to tantalum. Columbium getter pellets are approximately 3 to 5 mm dia by 3 mm long (EKW1). They are welded on to a molybdenum wire support in the vacuum tube. Heating is arranged by induction or electron bombardment and needs to be at 1650° C to degas the columbium and volatilize columbium oxide, and at 400° to 900° C for subsequent gas sorption.

Zirconium (melting point 1860° C) absorbs hydrogen to the extent of about 1500 times its own volume (at S.T.P.) when heated to 400° C (Fast, F9) and re-evolves it again at 880° C or more. Water vapour is cleaned up between 200° and 250° C. Furthermore, oxygen, nitrogen, carbon monoxide and carbon dioxide are taken up in quantities forming very stable solid solutions at a temperature of 1400° C. An efficient getter can therefore be arranged by means of two zirconium wires or strips, one at 400° C and the other at 1400° C. Ehrke and Slack (ES1) report, however, quite different results. They found that clean-up of hydrogen by zirconium began at 760° C and increased up to 1400° C, whereas nitrogen was only slightly gettered at 1530° C and the temperature required for oxygen was at least 885° C with the sorption rate increasing with temperature up to 1140° C. Furthermore, they did not record clean-up of other gases like carbon monoxide and carbon dioxide, whereas Fast indicates that all gases other than the noble gases were gettered. These large disparities may well be due to the presence of an oxide skin on the zirconium, which influences strongly the sorption. A preliminary heating of the zirconium to about 1200° C in a very good vacuum (10^{-6} torr) is essential for cleaning.

Reimann (R3) apparently supports the results of Fast (*i.e.* the temperature of 300° to 400° C for hydrogen and 1400° C for other gases) and suggests that the apparatus used by Ehrke and Slack employed greased taps which did not permit sufficiently clean conditions. Dushman (D1) reports the results of Guldner and Wooten's experiments conducted eight years after the Ehrke and Slack publication. They show that the optimum temperatures for zirconium in powder form on a molybdenum anode (degassed at more than 1000° C) are 400° C for oxygen, 300° C for hydrogen and 800° C for nitrogen, carbon dioxide and carbon monoxide. Furthermore, at '200° to 350° C, water vapour is cleaned up at about the same rate as oxygen'. Though these results uphold generally Fast's contentions, there are still disparities.

Zirconium is useful as a getter in the form of strip, wire or powder for some types of ultra-high frequency valves, for large transmitting valves and especially for operation in a mercury vapour atmosphere. Zirconium sheets or small tubes may be mounted on grid shields, cathode supports, etc., which are heated to 600° to 800° C during operation of the valve. Alternatively, a filament of 0·005 to 0·02 in. dia zirconium can be mounted separately and heated by direct passage of electric current. Espe, Knoll and Wilder (EKW1) report the use of zirconium wire, usually wound on a molybdenum mandrel, and run at 350° to 1700° C by connection in series or in parallel with the thermionic filament of an X-ray tube.

Another usual procedure is to spray or paint the zirconium powder in a binder (nitrocellulose in amyl acetate, the volatile constituents being subsequently evolved and pumped away during processing) on to the electrodes of a valve, *e.g.* the molydenum anode of a transmitting valve. If a colloidal silicic acid binder is used which is preheated to 1300° C in vacuum on a molybdenum anode, subsequent operation at 800° C is possible without gas evolution. Graphite anodes can also be similarly coated.

Zirconium hydride (ZrH_4) may also be applied to electrodes as a paste, by spraying or by catorophoresis (EKW1). The advantage compared with the use of pure zirconium is protection against atmospheric action during the sealing-in of the tube. At 800° C in vacuum, the hydrogen is released leaving the pure metal.

Titanium (melting point 1660° C). This metal has become increasingly available in the forms of wire and sheet, primarily as a consequence of the demand for it in the aircraft industry. In the solid form, it will sorb much greater quantities of hydrogen than will tantalum, this sorption beginning at a temperature of 375° C and increasing rapidly at temperatures above 400° C. It will also sorb (but to a considerably less extent) oxygen, nitrogen, carbon dioxide, carbon monoxide and some hydrocarbons (which will, however, tend to dissociate, *cf.* tungsten). Table 6.3 shows that the solubility of hydrogen is 40,740 cm^3 at 760 torr per 100 g of titanium at 20° C as compared with a figure of 4600 for tantalum and that the corresponding figures at 800° C are 14,090 for titanium and 250 for tantalum. Indeed, only the hydrides of lithium, sodium and calcium have a higher hydrogen content than titanium (Dushman, D1). The commercially available, vacuum-melted titanium contains on the average 0·008% of hydrogen by weight. As is pointed out by Holland (H16) this means that a gram of this metal is able to release $6{\cdot}5 \times 10^5$ litre of hydrogen at 10^{-6} torr; it is manifestly necessary to degas the metal thoroughly by heating *in vacuo* at about 1300° C before it can be used as a getter. It is the most important metal for use in getter-ion pumps (*see* § 7.5 where further data on sorption by titanium is given), where it is freshly deposited as a film on the interior of the cooled pump walls, in which form it has marked sorption properties for hydrogen and, to a lesser extent, oxygen, nitrogen, carbon dioxide, carbon monoxide and hydrocarbons. Like zirconium hydride, titanium hydride is used as a very effective getter, especially in some types of thermionic vacuum tube with metal envelopes. The hydrogen is released, leaving titanium on heating.

Thorium (melting point 1827° C). This metal sorbs oxygen by chemical reaction and also chemisorbs hydrogen and carbon dioxide, the best temperature range being 400° to 500° C. It is also used in a getter called Ceto getter which is an alloy of 80% Th with 20% misch metal (an alloy of cerium and other rare earth metals).

To use thorium powder (which is ignited readily by friction) it is coated on the appropriate part of the vacuum tube electrode or on a wire support and heated for two or three hours in a vacuum furnace to a temperature of 800° to 1000° C for nickel and 1500° to 1600° C for graphite (EKW1).

Ceto powder (which is very inflammable) is made into a paste with amyl acetate and painted or sprayed on to the electrode concerned, which is then sintered in vacuum. It is degassed at 800° C and getters efficiently at temperatures above 80° C with a maximum rate at 200° to 500° C. It is chiefly of use when it is necessary to reduce secondary emission from the electrode as compared with that which might prevail if a barium getter were adopted.

Tungsten (melting point 3382° C) and **Molybdenum** (melting point 2620° C). These metals are not normally employed as bulk getters except in some specialized ultra-high vacuum systems but their gas absorption properties are of importance because they are frequently used (especially tungsten) as heated filaments in vacuum tubes.

Oxygen is chemisorbed on heated tungsten. At moderate temperatures, this sorption of oxygen will decrease the thermionic emission to 10^{-2} to 10^{-5} of its value for pure tungsten and it is only by heating to above 1700° C that the sorbed gas is released and the full emission restored. Langmuir (L10) has shown that a fraction of the oxygen molecules incident upon tungsten heated to temperatures above 1000° C and at pressures below $7{\cdot}5 \times 10^{-2}$ torr react with the tungsten to form WO_3 which, however, evaporates as fast as it is formed. As the tungsten oxide is a solid of low vapour pressure which is deposited on the vessel walls, the oxygen pressure will be reduced in the presence of a tungsten filament, *i.e.* a pumping action for oxygen takes place (§ 6.16). Langmuir also established that nitrogen and carbon monoxide are cleaned up by heated tungsten. Nitrogen is sorbed at a constant rate at filament temperatures of 2230° to 2530° C over the pressure range from about $7{\cdot}5 \times 10^{-2}$ to 2×10^{-3} torr. At low pressures the nitrogen does not attack the filament, but is sorbed by virtue of the evaporation of tungsten, which will, of course, increase with temperature. At pressures below 2×10^{-3} torr, the volatilized tungsten atoms can travel to the walls without encountering many gas molecules so the sorption rate for nitrogen decreases, though the tungsten will combine with nitrogen adsorbed on the vessel walls if these are cooled with liquid air (Dushman, D1). Carbon monoxide behaves similarly to nitrogen in the presence of heated tungsten (Langmuir, L11). In the case of hydrogen, dissociation of some of the molecules into atoms takes place if incident on tungsten (or other metal, *e.g.* molybdenum, platinum or palladium) heated to above 1250° C. The degree of dissociation is very small at atmospheric pressure, but increases by about 25 times on reducing the pressure to 1 torr, and also increases noticeably with increase of temperature. Thus, at a pressure of 1 torr, 1 in 180 molecules of hydrogen are dissociated at a tungsten filament temperature of 1330° C, 1 in 4 approx at 1930° C and 94% at 2730° C. The atomic hydrogen is strongly chemically reactive and is readily sorbed by the glass walls of the containing vessel, though most of the atoms recombine on adsorption to re-form molecules which are not strongly bonded to the surface. Chlorine also dissociates similarly on contact with heated tungsten and so does oxygen, but to a much smaller extent because of its high dissociation energy. Indeed, many gaseous compounds such as water vapour, hydrocarbons and, in particular, pump oil vapours will dissociate; water vapour, for example, will give oxygen which combines with the tungsten whilst the hydrogen is evolved. The tungsten oxide will then evaporate to the walls, where it will be reduced to the metal by the atomic hydrogen formed, a reaction which will also result in water vapour being produced again. On dissociation of hydrocarbons, tungsten carbide is formed.

Molybdenum reacts chemically with oxygen, chemisorbs hydrogen, C_2H_2 and C_2H_4, and sorbs nitrogen and carbon monoxide. In the case of nitrogen and carbon monoxide, Langmuir (L11) concludes that the evaporated molybdenum atoms (at temperature above 1700° C) combine chemically with the gas molecules on collision, but that the presence of even very small partial pressures of water vapour (present, for example, if the vessel is not baked when under vacuum) inhibits the sorption of nitrogen whilst it enhances the sorption of carbon monoxide.

A useful table given by Espe, Knoll and Wilder (EKW1) gives summarized details of the degassing, flashing and operating temperatures of a variety of getters and also indicates their applications. This data is reproduced here as Table 6.16.

Clean-up in Ionized Gases

6.14. Sorption and Electrical Clean-up in a Gaseous Discharge

If a gas within a container is ionized, *e.g.* in a cold-cathode discharge, or by the electrons from a hot cathode, or even in an electrodeless discharge, the positive ions will travel to negatively charged electrodes or to a glass wall (which is usually negatively charged, *see* § 6.16) and may be retained by surface forces or, in some cases, may diffuse into the solid and be held in solution. The gas pressure within the container will therefore decrease, provided that the rate of sorption of ions is greater than the rate of desorption due to outgassing of the constructional materials and assuming, moreover, that if connected to a pump, the container does not receive molecules of gas or vapour due to back-diffusion or back-streaming.

That this clean-up action will take place in a gaseous discharge at low pressures was first observed in 1858 by Plücker (P9) and is a well-known phenomenon in, for example, the cold-cathode type of 'soft' X-ray tube. It will also occur in the Penning gauge (§ 3.10) and other cold-cathode ionization gauges and in hot-cathode electron tubes such as thermionic valves and, in particular, in the hot-cathode ionization gauge. Indeed, in ionization gauges of both the cold and hot cathode types, this clean-up is a source of difficulty in accurate pressure measurement (§ 3.9) but has, however, been put to effective use in the production of ultra-high vacua (Chapter 8).

It cannot usually be assumed that this pressure reduction which can take place in a gaseous discharge is due solely to the removal of some of the ions at the electrodes or a glass wall (*i.e.* electrical clean-up proper) as other phenomena resulting in sorption may occur. In cold-cathode discharges these other phenomena are:

(*a*) Sorption (indeed, gettering) of both neutral molecules and ions by the film of the cathode metal which may be sputtered (*see* § 10.10) on the surfaces within the container. This is particularly likely at gas pressures between 5×10^{-4} and 5×10^{-1} torr, increases rapidly with potential differences across the anode and cathode of above 500 V, and with the discharge current. Moreover, electrodes of silver, gold, copper, platinum, nickel and iron will have sputtering rates in descending order whereas aluminium will normally hardly sputter at all.

(*b*) Gas molecules and ions may react mechanically (adsorption) or chemically with the electrodes and/or envelope. Of the common glasses, the soda-lime ones are the most reactive.

TABLE 6.16

Degassing, flashing and operating temperatures of typical getters

Material	Ta	Cb	Zr	Th	Ceto	Mg	Al–Mg	Ba and Ba compounds	Reaction-type Getters			Phosphorus
									Bato	Batalum	Ba-beryllliate	
Form of application	Bulk Coating	Bulk	Bulk Coating	Coating	Coating	Flash	Flash	Flash	Flash	Flash	Flash	Flash
Form of getter	Sheet Powder	Pellets	Sheet Wire Powder	Powder	Powder	Ribbon Wire	Powder Paint	Metal-clad wire pellets	Ni-clad pellets	$BaCO_3$ paint on Ta	$BaBeO_2$ paint on Ta	Powder suspension
Degassing preheating temperature (°C)	1600–2000	1650	700–1300 (up to 1700 in compound wires)	For metal base 800–1000 (for graphite 1500–1600)	800–1200	400	400	600–700	No ref	800–1100	900–1000	No ref
Flashing temperature (°C)	—	—	—	—	—	500	No ref	900–1300	750–800 (900)	1200–1300	1300	> 200
Operating temperature (°C)	700–1200	500	800 (up to 1600 in compound wires)	400–500	200–500	Absorbs gases only during flashing		20–200 max	20–200	20–200	20–200	100–200
Applications reported	D, E, M	D, E	C, D, E, F, I, K, L, M, N	C, D	P	I, K	A, F	A, B, D, F, G, H, I, (L), N	D, M	A, F	A, F	O

A—Small receiving tubes
B—Miniature tubes
C—UHF tubes
D—Medium size transmitting tubes
E—High power transmitting tubes
F—Oxide cathode tubes
G—Cathode-ray tubes
H—Phototubes
I—Gaseous-discharge tubes
K—Hg-vapour tubes
L—X-ray tubes
M—High power vacuum tubes
N—Tubes with thoriated cathodes
O—Incandescent lamps
P—Vacuum tubes in which neither flashing getters nor the high temperatures necessary for Ta and Zr may be used

(*c*) Ions may react chemically with molecules with which they collide; this is outside the meaning of the term and not a usual source of clean-up.

In addition, in hot-cathode discharge devices, collision of gas molecules or ions with the hot cathode may result in sorption or dissociation, as discussed in § 6.13. Furthermore, during any degassing of the electrodes by induction-heating or electron-bombardment or direct heating of a filament, thin metallic films, which have some gettering action, may be deposited on the cooler surfaces within the container.

6.15. Clean-up in a Cold-cathode Gaseous Discharge

Alterthum, Lompe and Seeliger (ALS1) studied the clean-up of the inert rare gases argon, neon and helium and report that the rate increases considerably with decrease in pressure down to 3 torr, when it becomes approximately independent of the pressure, that this rate is proportional to the discharge current and independent of the length and form of the discharge tube, and that most of the gas is sorbed as a result of positive ions being driven into the cathode under the action of the electric field, *i.e.* electrical clean-up.

Recent work on clean-up in cold-cathode discharge tubes has mostly been concerned with ionization gauges of the Penning type. The conclusion is that the gas sorption is primarily due to electrical clean-up. Leck (L12) used a gauge of the Penning and Nienhuis design (§ 3.10) with an anode 2 cm long and 2 cm internal dia and end plates of slightly larger diameter fitted to give a gap of 0·3 cm between each end plate and the anode. This arrangement meant that the discharge was screened from the Pyrex glass envelope, so that it is not surprising that no sorption effect due to the glass was obtained. Indeed, at the potentials used in Penning type gauges (< 500 V) it is probable that the glass wall contributes little to the clean-up, even if not shielded. The sorption of air recorded by Leck is shown in Fig. 6.7. The gauge sensitivity was independent of the magnetic field strength over the range from 250 to at least 2000 oersted.

These characteristics (Fig. 6.7) are of a form typical of results obtained also for nitrogen, hydrogen, argon, water vapour, ethyl ether and carbon tetrachloride, except that saturation was obtained more readily for argon and hydrogen. The sorption ceased as soon as the discharge was switched off except in the case of ethyl ether for which sorption continued for about a further 20 min, probably due to take up of this vapour by a film of sputtered nickel from the cathode. For argon and hydrogen, the steady state value of the rate of clean-up was considerably less than for the other gases and only about 5% of that for air. The curves shown in Fig. 6.7 were obtained immediately after a degassing bake of 5 to 10 min at 400° C. Without degassing, the initial clean-up rate was less, but the final steady rate was found to be independent of the baking process.

When the discharge was switched off, the desorption rate was never more than 1% of the previous sorption rate. On baking the glass envelope at 400° to 500° C with the discharge on, however, a large burst of gas appeared, the pressure rising suddenly from about 10^{-5} to 10^{-2} torr and subsequently falling again. The total amount of desorbed gas was probably the same as the amount previously sorbed.

In subsequent work using the same type of Penning–Nienhuis gauge and with a mass spectrometer attached to the vacuum system so that the constituent gases could be analysed, Brown and Leck (BL1) studied successive sorption and desorption of gas in an initially baked-out (400° C) tube. The discharge was run in a particular gas for a certain time to cause sorption; this gas sample was removed from the gauge and then a second gas introduced and the discharge restarted. This second discharge caused the first sorbed gas to be released, so that the gas composition in the discharge changed. Desorption by discharge was observed for helium, neon, argon, krypton, hydrogen, nitrogen, oxygen and carbon dioxide. The observations made may be summarized as follows:

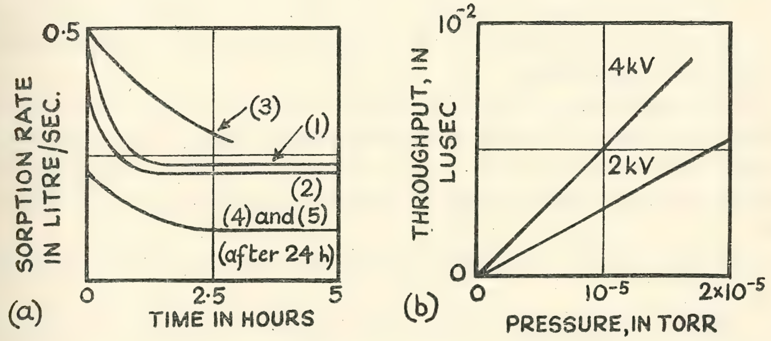


FIG. 6.7 Sorption of air in a Penning–Nienhuis gauge with nickel electrodes

(*a*) The rate of clean-up per unit pressure (litre per sec) at constant pressure

Curve (1) pressure 2×10^{-5} torr
Curve (2) pressure 5×10^{-5} torr } anode-cathode p.d. = 4 kV
Curve (3) pressure 5×10^{-6} torr
Curve (4) pressure 2×10^{-5} torr } anode-cathode p.d. = 2 kV
Curve (5) pressure 1×10^{-5} torr

(*b*) The initial rate of sorption as a function of pressure at 2 kV and 4 kV

(*i*) The rate of degassing of the sorbed gas by the discharge did not depend appreciably on the applied voltage (between 500 and 4000 V), the magnetic field strength (300–600 oersted) or the gas in the discharge with the exception of hydrogen.

(*ii*) A discharge in hydrogen was comparatively inefficient at releasing the sorbed gas.

(*iii*) The desorption rate was dependent on the discharge current, but the total quantity of gas recovered was independent of this current, *i.e.* for a smaller current a correspondingly longer time was necessary to produce the same recovery of gas.

(*iv*) Significant clean-up only took place in the presence of a discharge; the operation of the discharge increased the clean-up rate by at least four orders of magnitude. This means that sorption was due to electrical clean-up and that the contribution due to other phenomena was negligible.

(*v*) Desorption of the sorbed gas was negligible at room temperature even over a period of 24 hours. However, in the case of hydrogen and helium, desorption by discharge in a second gas after a wait of 24 hours gave only 50% of the gas expected.

(*vi*) Sorbed gas could be released by heating instead of the discharge: at 100° C desorption was just detectable; at 200° C, total desorption took place in 20 min, giving the same amount of gas as would have been obtained by running a second discharge.

(*vii*) On induction-heating the cathodes to 1000° C whilst the anode and glass envelope were at a temperature not greater than 50°, it was shown that virtually all the gas was taken up by the cathodes. After a few seconds of such heating, no further gas could be released by a discharge, *i.e.* ion bombardment.

(*viii*) Similar results were obtained for nickel, molybdenum and aluminium electrodes.

(*ix*) With an initial pump-down and bake-out period of 24 hours, the operation of the discharge caused continuous desorption of water vapour from the gauge; this desorption fell to zero, however, if the gauge electrodes were initially degassed by induction-heating to dull red (800–900° C).

Brown and Leck conclude that, as the sorption and desorption are virtually independent of the chemical nature of the gas or the cathode metal, the positive ions which reach the cathode become neutralized there and are retained by Van der Waal surface forces. The ease with which desorption is possible supports this contention. The chance of an ion 'sticking' on a clean surface approached 100% for many gases. The maximum quantity of sorbed gas recovered on a subsequent discharge or heating was shown to correspond approximately with that required to form a complete monolayer on the cathode. If a positive ion impinges on a gas-covered cathode, then it probably dislodges an adsorbed molecule and becomes adsorbed itself.

In view of the fact that physical adsorption of the inert gases occurs only at temperatures below −80° C Brown and Leck suggest that it is difficult to understand why *ionized gas* is adsorbed and retained up to temperatures of 100° C. This is surely due to the fact that the positive ions impinge on the cathode from the discharge at energies of 500 eV and more, whereas molecules will have only thermal energies of about 0·025 eV at 20° C. It seems, therefore, that the accelerated ions will be embedded in the surface layers of the cathode metal more effectively than molecules would be. Though physical adsorption might prevail in both cases, the true issue would seem to be to define what is meant by the surface of the electrode in these circumstances.

6.16. Electrical Clean-up in a Hot-cathode Discharge

When thermionically emitted electrons are accelerated to an anode at a potential above the ionization potential of the gas within a container, positive ions of the gas are produced and will travel to the cathode or negatively charged electrodes. A glass envelope will become slightly negatively charged, *i.e.* it will be near the cathode potential and therefore attract positive ions—because glasses have secondary emission coefficients less than unity for the range of incident electron energies up to 40–50 eV, but for incident electron energies between about 40 eV and 2400 eV, the glass has a secondary electron emission coefficient greater than unity, and will therefore tend to become positively charged. On arrival at a surface, the ionic charges will be neutralized by free electrons and the neutral molecules resulting will have a distinct probability of being retained, particularly if these surfaces have been previously degassed. There will consequently occur a certain rate of decrease of the gas pressure within the container.

Most of the recent work in this field has been at total gas pressures below 10^{-4} torr, and most of the important results have been obtained using hot-cathode ionization gauges, primarily because of the application of ion pumping to the production of ultra-high vacua (Chapter 8). Similar considerations often apply in the normal operation of sealed-off thermionic vacuum tubes, though, in this case, reduction of the pressure after seal-off is chiefly due to the getter.

Schwarz (S19) studied experimentally the clean-up of hydrogen, nitrogen and argon in an initially degassed hot-cathode ionization gauge of conventional geometry (outer cylindrical ion collector of nickel at −5 V, inner cylindrical nickel grid at +110 V and axial tungsten filament). In the case of hydrogen, the pressure decreased from $1{\cdot}55 \times 10^{-3}$ to $1{\cdot}5 \times 10^{-5}$ torr in 3 min because of dissociation of the hydrogen at the hot filament (*see* § 6.13), the grid and collector potentials being zero. In this case, this rate of sorption was much more rapid than any electrical clean-up rate proper with an electron current of 1 mA. Clean-up of oxygen and argon were only recorded if the grid and collector potentials were applied and it was suggested that most of the gas goes to the glass wall.

Subsequent work by Alpert and others has been mostly with the Bayard–Alpert type of ionization gauge (§ 3.9) able to record pressures some 100 times lower than the conventional gauge.

In his excellently planned experiments on the production of ultra-high vacua (Chapter 8) Alpert (A10) first pumped and degassed thoroughly a Bayard–Alpert gauge to attain a pressure of about 5×10^{-8} torr, isolated this gauge from the pumps by his metal ultra-high vacuum valve (§ 5.9) and then reduced the pressure within the gauge to 10^{-10} torr and even lower by the clean-up action obtained on applying the electrode potentials. In this gauge pumping action, Alpert followed Schwarz in distinguishing two mechanisms: (*a*) electrical clean-up due to the transport of positive ions to a negatively charged collector (or the walls), and (*b*) chemical clean-up due to reaction of active gas constituents (*e.g.* hydrogen) with the hot filament. By analogy with the equation for the speed of a conventional pump, the rate of change of pressure, $\frac{dp}{dt}$, at a pressure p at time t due to electrical clean-up is given by

$$\frac{dp}{dt} = -\frac{S_E}{V}(p - p_u) \tag{6.9}$$

where S_E is the **electrical pumping speed**, V is the volume of the enclosure and p_u is the ultimate pressure obtained by this means.

The solution of this equation is:

$$p = p_u + (p_o - p_u)\exp\left(-\frac{S_E}{V}t\right) \tag{6.10}$$

where p_o is the initial pressure at time $t = 0$.

An expression similar to equation (6.9) for the **chemical pumping action** holds so that the total rate of reduction of pressure is given by:

$$\frac{dp}{dt} = \frac{-S_E}{V}(p - p_u) - \frac{S_C}{V}(p - p_c) \tag{6.11}$$

where S_C is the chemical pumping speed and p_c is the ultimate pressure obtainable by chemical pumping alone.

For gases which are chemically inert to the heated tungsten filament, S_C is zero and equation (6.9) applies.

Alpert then assumes that every ion collected is permanently retained at the collector, *i.e.* removed from the gas space. This assumption has been criticized, as shown on p. 290, but disregarding these criticisms in this context, equation (6.9) can be written in the form:

$$S_E = \left(-V\frac{dn}{dt}\right)/n \tag{6.12}$$

where n is the number of molecules per unit volume at the pressure p. Here p_u in equation (6.9) has been neglected in comparison with p_o; this presumption is justifiable in calculating the initial pumping speed as experiment shows that p_u is not more than $0{\cdot}01p_o$.

To calculate S_E for an ionization gauge, suppose the positive ion current is 10^{-x} amp at a nitrogen pressure of 10^{-3} torr for an electron current of 1 mA. Assuming a linear relationship between ion current and pressure (justified experimentally by Alpert down to a pressure of 10^{-10} torr), then the ion current at a pressure of 10^{-m} torr is $10^{-(m+x-3)}$ amp. If each ion is singly charged (electronic charge $= 1{\cdot}6 \times 10^{-19}$ coulomb), the number of ions which reach the ion collector per second is $6 \times 10^{18} \times 10^{-(m+x-3)}$, which is $\frac{dn}{dt}$. At a pressure of 10^{-m} torr, the number of molecules per litre is n, equal to $3{\cdot}5 \times 10^{19} \times 10^{-m}$ (*see* Appendix A). Substituting for $\frac{dn}{dt}$ and n in equation (6.12) gives:

$$S_E = 1{\cdot}7 \times 10^{-(x-2)} \text{ litre/sec} \tag{6.13}$$

An expression for the chemical pumping speed is readily derived on the assumption that every molecule of gas which reacts with the hot filament is, in effect, removed from the gas space (which is not necessarily or, indeed, usually the case). If the surface area of the hot filament is A, then from Knudsen's equation in the kinetic theory of gases (*see* Appendix A),

$$N = \frac{n^*\bar{v}}{4} \cdot A$$

where N is the number of molecules which impinge per second on the filament, n^* is the number of reactive gas molecules per unit volume (a number often unknown in practice) and $\bar{v}$ is the mean molecular velocity at the temperature of the gas. If V is the volume of the enclosure,

$$N = -V\frac{dn^*}{dt}$$

and

$$S_C = \left(-V\frac{dn^*}{dt}\right)\frac{1}{n^*} = \frac{\bar{v}A}{4} \tag{6.14}$$

which will be in the units cm³ per sec if A is in cm² and $\bar{v}$ is in cm sec.$^{-1}$.

However, this equation usually gives an over-estimate of the pumping speed. For example, in the case of oxygen in the presence of a hot tungsten filament (§ 6.13), tungsten oxide (WO_3) evaporates off as fast as it is produced on a filament at a temperature above 1000° C and there is a consequent rate of reduction of the oxygen pressure. But only a fraction of the oxygen molecules reacts with the tungsten, this fraction being 0·001 at 1000° C, 0·01 at 1300° C 0·025 at 1500° C, 0·1 at 2000° C and 0·15 at 2500° C. (Langmuir, L10, L11.)

In an experiment with a Bayard–Alpert gauge of volume 0·8 litre pumped initially to 7×10^{-7} torr and then isolated from a mercury diffusion pump by a greaseless glass valve (§ 5.10), Baker and Yarwood (BY1, *see also* Yarwood, Y4) obtained the pressure against time curve shown in Fig. 6.8 on running the gauge at its normal operating potentials and with an electron current to the positive grid of 1 mA.

As shown previously by Bloomer and Haine (BH1), this curve has two fairly distinct regions A and B where for the region A the value of $\frac{dp}{dt}$ at the mid-point of the curve is about 15 times greater than the mean value for region B. Considering first only the rate of change of pressure over the region A, this is $-1{\cdot}2 \times 10^{-7}$ torr per min at a mean pressure of 4×10^{-7} torr, so that the pumping speed S is given by

$$S = \frac{-V}{p}\frac{dp}{dt} = \frac{0{\cdot}8}{4 \times 10^{-7}} \times \frac{1{\cdot}2 \times 10^{-7}}{60} = 4 \times 10^{-3} \text{ litre/sec}$$

This gauge had a sensitivity for air of $1{\cdot}3 \times 10^{-5}$ amp/mA/10^{-3} torr. The calculated electrical pumping speed is therefore given by equation (6.13) as:

$$S_E = 1{\cdot}7 \times 1{\cdot}3 \times 10^{-3} = 2{\cdot}2 \times 10^{-3} \text{ litre/sec}$$

because $x = 5$ in this case.

The measured pumping speed is therefore nearly twice the simply calculated value. Young (Y5) found this ratio for nitrogen to be four. This disparity is probably due to three causes:

(*i*) The measured positive ion current is only that reaching the negatively charged ion collector whereas positive ions will also travel to the negatively charged glass wall, and the corresponding ion current due to these latter ions is not recorded by the circuit meter. Young (Y5) measured the ion current to the wall and found it to be 5 to 10 times the current to the collector electrode.

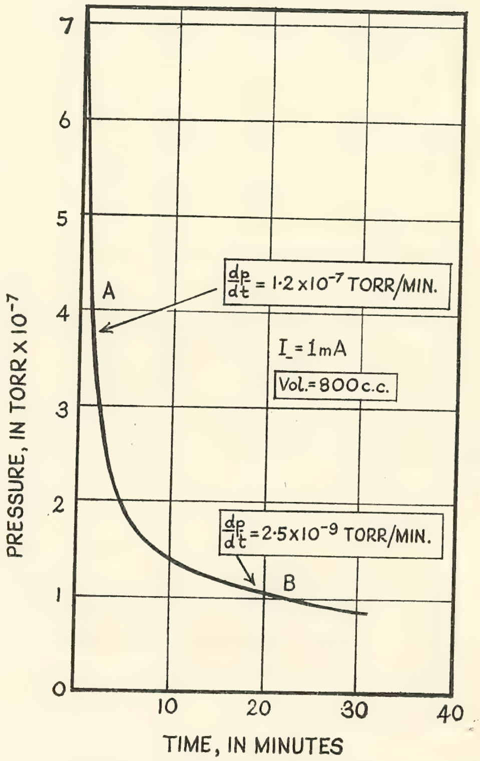


FIG. 6.8 Reduction of pressure in an ionization gauge of the Bayard–Alpert type which is isolated from the diffusion pump by a greaseless glass valve; initial pressure 7×10^{-7} torr

(*ii*) The gauge sensitivity for air is assumed; the residual gases within the gauge at the initial pressure in the experiment are not likely to be the same as in air; moreover, it is probable that, during the electrical pumping, the relative proportions of the constituent gases will alter.

(*iii*) Whilst ions are being sorbed during electrical clean-up at the ion collector and the glass walls, desorption of molecules from these surfaces may occur. This desorption increases as more and more gas is collected at the sites to which it is removed, leading eventually to a smaller rate of decrease of pressure with time, as is shown in the region B of the curve.

(*iv*) Sorption of some constituents of the residual gases at the heated tungsten filament is neglected.

Considerable research has been undertaken in recent years—and is still being actively pursued—on the mechanisms involved in electrical clean-up of gases in both cold- and hot-cathode discharge tubes. The objects of these investigations are to arrive at optimum rates of clean-up in relation to tube electrode disposition, and geometry and electrical parameters, to establish the sites to which ions are transported, to study the sorption and desorption of ions and molecules at these sites and times of retentions, to compare the influence of envelopes of various glasses as compared with Aquadag and metal-coated glasses and also of metal envelopes, to provide data on the influence of the nature of the residual gas, the range of gas pressures from the initial to the final values, the effects of superimposed magnetic fields and so on. Many disparities exist between the present results given by the various investigators. Further data is given in Chapters 7 and 8 in regard to practical considerations involved in the design of ion pumps, ion-sorption pumps, getter-ion pumps and in ultra-high vacuum technology. *See also* Dushman (D1), Schwarz (S19), Alpert (A10), Bloomer and Haine (BH1), Young (Y5), Varnerin and Carmichael (VC1), Adam (A11), Leck (L12), Robinson and Berz (RB1) and Trendelenburg and Carmichael (TC2).

7

ION PUMPS AND GETTER-ION PUMPS

7.1. Terms Used

There are differences between the recommendations of the British Standards Institution (B.S.2951: 1958, *Glossary of Terms Used in High Vacuum Technology*) and those of the Committee on Standards of the American Vacuum Society (*Glossary of Terms Used in Vacuum Technology*, 1958). The B.S.I. recommend the term 'ionization pump', defined as 'a vacuum pump in which gas molecules in a vacuum system are ionized and transported in a desired direction by an electric field'. There are, however, two main types of ion pump, both of which utilize an electric field (and, in some cases, also a magnetic field) to give a preferred direction to ions: in one of these, ions are transported to an auxiliary pump or trap, and in the other the ions are driven into a sorbent. The American Vacuum Society recommend the term **ion pump** for the former type and the term **ion-sorption pump** for the latter. These American terms will be used here, though it must be said that, in some instances, it is not a straightforward matter to classify a pump in one or other of the two categories. Furthermore, a 'gettering pump', according to B.S.I., is a 'vacuum pump whose action is due to continuous or intermittent gettering'. Again the American recommendations are to use two terms: (*a*) **sorption pump**, which is a 'pump with a renewable trapping surface which reduces the partial pressure of gases by adsorption, absorption or chemisorption' and (*b*) **getter-ion pump**, as a class of ion-sorption pump in which the continuous or intermittent vaporization of a getter gives a fresh condensed deposit on a trapping surface at which the gas is sorbed. The American terms will be used here.

Those types of pump which have received most attention in recent work and which are being applied to specialized problems of gas removal in vacuum systems are: (*i*) the ion pump, (*ii*) the ion-sorption pump, (*iii*) the getter-ion pump. The chief purposes of these pumps are (*i*) to provide a high vacuum or ultra-high vacuum in a chamber free of the back-streaming products associated with the use of diffusion pumps, or (*ii*) to establish a lower pressure in a chamber than is possible by diffusion pumps.

7.2. Ion Pumps

Pumps in which some of the gas is ionized and then impelled by an electric field towards a fore-vacuum created by a rotary pump, where the ions are neutralized and ejected to the atmosphere, have been designed by Schwarz,

and by Foster, Lawrence and Lofgren. Sorption of ions/molecules at the interior surfaces also occurs in these pumps.

Schwarz (S20) has investigated theoretically the possibility of transporting ions along a cylindrical tube to provide a pumping action. He concludes that very large electron currents in a tube of excessive length would be necessary to obtain sufficient ions by collision in a straightforward d.c. discharge maintained between a pair of electrodes, and that space-charge effects, ionic recombination and loss of electrons to the walls would all add to design difficulties. The solution suggested is therefore to increase the electron paths very considerably without increasing the necessary tube length. Two ways of doing this are (*a*) to make the electrons oscillate in screw paths in the axis of the discharge tube and (*b*) to confine the electrons in spiral paths within a system of cylindrical electrodes by the use of a magnetic field. Schwarz consequently constructed the ion pump (called by him an 'electronic pump') shown here in Fig. 7.1.

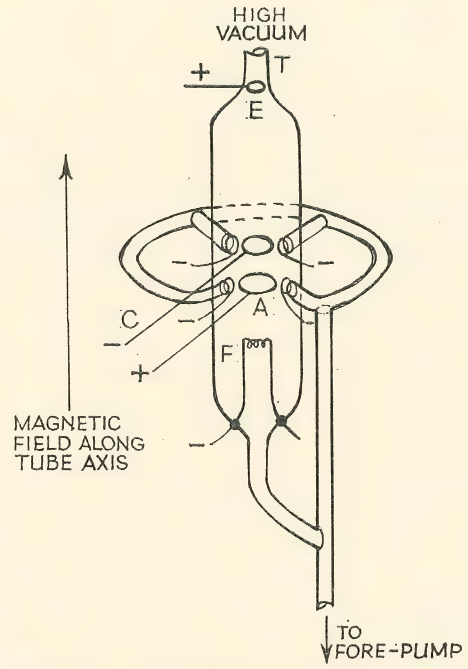


FIG. 7.1 Ion pump due to Schwarz

In this ion pump, electrons emitted from the heated tungsten filament *F* are accelerated towards the ring-shaped anode *A* within a glass tube which is initially evacuated to about 10^{-3} torr by a rotary fore-pump. A third annular electrode *C* is at the filamentary cathode potential. With the anode at 2 kV with respect to *F*, an electron current of about 10 mA is produced and the electrons oscillate many times back and forth through the anode before collection. To minimize premature collection of these electrons, *i.e.* to ensure that the number of oscillations of the electrons about A is as large as possible, a magnetic field is arranged parallel to the tube axis to confine the electrons to spiral paths near this axis. The positive ions produced are mostly transported to the four slightly negative ring-shaped electrodes at the entrances to the four port-holes spaced around the tube walls at a level between the electrodes A and C but nearer to A. Tubes to these port-holes connect as shown in the diagram to the single tube leading to the rotary fore-pump. The vessel to be evacuated is connected to T at the top of the ion pump. Another ring electrode E, at the entrance to this top connection, is maintained at a positive potential to prevent positive ions from reaching the vessel undergoing evacuation.

With a vessel of volume 0·5 litre connected at T, this ion pump reduced the pressure (as recorded by an ionization gauge) from 10^{-3} torr (the fore-pressure) to 10^{-5} torr, and sometimes 5×10^{-6} torr, in less than one second. This pump-down was repeated 30 times without any saturation of the pump being observed. As even threefold repetition would cause a monolayer of molecules to form on the glass wall, it was concluded that the positive ions were not simply being sorbed at this wall but were indeed being transported to the fore-pump. The pumping speed was determined to be 2·5 litre per sec.

In a later model, Schwarz (S21) introduced a cylindrical net electrode a few millimetres within the glass wall between the electrodes A and C and maintained at a slightly negative potential, and also yet another annular electrode at cathode potential near the filament F. A speed of 10 litre per sec was then obtained in a pump of tube radius 1 cm and an ultimate pressure of 2×10^{-7} torr.

The ion pump described by Foster, Lawrence and Lofgren (FLL1) is much larger (Fig. 7.2) and is based on a metal tube over 12 ft in length and of internal diameter 6 in. A rotary fore-pump is used to evacuate this tube initially to about 5×10^{-4} torr. At one end of this tube is a hollow hot cathode (radiantly heated tungsten disc) and at the other end a hollow cold cathode. These cathodes are at −300 V with respect to the tube itself, which is earthed and acts as an anode. To ensure that electrons emitted from the hot cathode are confined to tight helical paths along the axis of the tube, the whole length is surrounded by a magnetizing coil; however, to allow the necessary wide bore inlet to the pump at the centre of the tube, this magnet is in three parts: two similar sections to the left and right of the inlet port and a water-cooled open helical winding within this inlet port region. Electrons emitted from the hot cathode will then traverse the axial region of the tube, be reflected at the cold cathode at the far end, be returned to and reflected again at the hot cathode and so on. They will therefore oscillate backwards and forwards in the tube and lose energy by exciting and ionizing the residual gas molecules until they are eventually collected by the anode. The positive ions created will move slowly compared with electrons in the discharge and hence build up a positive space-charge which impels the positive ions towards the cathodes. At the cathodes, some of the reactive gas ions are chemisorbed, others are neutralized and returned to the discharge. Those neutral molecules

returned may enter the fore-vacuum region (the fore-pump tubulation is connected to the main ion pump tube in the vicinity of the hot cathode) or may be ionized again. Also, the cathode material will sputter (§ 10.10) on to the neighbouring surfaces and the metal film formed can trap some gas.

The discharge current needs to be 10 to 20 amp at 300 to 400 V for high speed pumping. At low pressures in the central region of the pump, the supply of positive ions is inadequate to maintain such a discharge unless gas is leaked into the hot-cathode region to maintain there a pressure above 3×10^{-4} torr. To confine this increased pressure to this region, the anode constriction tube shown in the diagram is necessary. As the diameter of this constriction tube is only slightly larger than the width of the discharge, gas which might have diffused through this tube is instead ionized and returned to the cathode region.

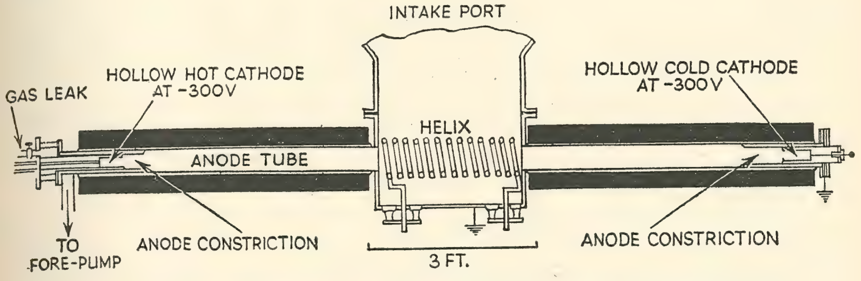


FIG. 7.2 High speed ion pump due to Foster, Lawrence and Lofgren

The pressure at the exit to the fore-pump is maintained usually at 3 to 5×10^{-4} torr but 10^{-2} torr has been used, though this higher pressure will tend to shorten the life of the cathode because of positive ion bombardment.

The factors which contribute to the ultimate pressure as gas entering the pump inlet is ionized and transported to the fore-pump, are outgassing of the surfaces, ions which leave the discharge and become neutralized on the metal surfaces near the centre section, and also those (the majority) which migrate to the ends of the main pump tube and are neutralized on the walls of the anode constriction tubes. These latter molecules will tend to diffuse back towards the pump inlet but this back-diffusion is reduced by making the main pump tube long enough to ensure a high probability that these molecules will be re-ionized before reaching the pump inlet at the centre. There exists also the probability that neutral atoms are formed in the discharge but this is small except at low gas pressures and high density of ions.

By an optimum choice of the pump dimensions in relation to the cathode current and the operating potentials, these sources of back-diffusion were reduced to the extent that the pumps could be used to evacuate a 48,000 litre tank from a fore-pressure of 10^{-2} torr to a final pressure of 5×10^{-5} torr and, in some cases, 5×10^{-6} torr.

Approximate operating conditions recorded for this pump were: pumping speed, 3000 to 7000 litre per sec; ultimate pressure, 8×10^{-7} torr to 5×10^{-6} torr (presumably with an ionization gauge connected directly to the sealed inlet, *i.e.* without a tank undergoing pumping); arc voltage, 300 to 400 V; arc current, 10 to 20 amp; cathode power, 4·5 kW; magnetic power: side magnets, 20 kW; centre helix, 12 kW, with a current of 5000 amp; fore-pressure, 3×10^{-4} to 10^{-2} torr.

This pump can be operated with the fore-pump isolated provided that the inlet gas flow is not more than 0·02 cc at S.T.P. per sec, as this amount of gas is removed by chemisorption and adsorption alone, unless the gas concerned is inert.

As compared with a conventional vapour pump, the advantage afforded is freedom from backstreaming of pumping fluid without a cold trap or baffle being necessary. Indeed, when the pump was operated for a day with the fore-pump isolated, the difference between the readings of an ionization gauge which was trapped compared with one untrapped was less than 10%. It is unlikely, however, that this type of pump will replace the vapour pump with its comparatively very simple electrical circuit and power demands, except for use in specialized research equipment, *e.g.* large particle accelerators. Even in such cases, its chief rival, the getter-ion pump (§ 7.5) shows greater promise at the present time.

7.3. Ion-sorption Pumps

In this category, the use of an ionization gauge (or modified ionization gauge) as a pump (§ 6.14) is the technique which has received most attention and application in recent years, especially in order to obtain ultra-high vacua (Chapter 8). Whether such pumps should be classified as ion pumps or as ion-sorption pumps depends on whether the electrode or glass walls to which the ions are impelled is regarded as a trap or as a sorption device. Here it will be regarded as a sorption (including adsorption) device.

Following on the work of Blears (B5), Riddiford (R16) and Schwarz (S19), the chief exponent of the use of the ionization gauge as a pump has been Alpert and his co-workers, who first produced a vacuum of the order of 5×10^{-8} torr in a hot-cathode ionization gauge of the Bayard–Alpert design (§ 3.9) by means of a fractionating oil-diffusion pump, isolated the gauge from the diffusion pump by an ultra-high vacuum valve (§ 5.9) and then reduced the pressure within the gauge to 10^{-10} or even 10^{-11} torr by the subsequent pumping action of the gauge. This technique and variations of it are described more fully in Chapter 8.

The pumping actions of the cold- and hot-cathode ionization gauges have been discussed in §§ 6.15 and 6.16; in their application as pumps important points are (*i*) it is essential to degas the gauge envelope initially by baking (450° C for 4 hours or more) and the electrodes by induction-heating or electron bombardment (1200° C for 1 hour); (*ii*) in the hot-cathode gauge, the heated filament will sorb reactive gases (§ 6.13); (*iii*) in general, the ionization current at a given pressure will be greater in the cold-cathode gauge than in the hot-cathode type, so the former gauge has the greater pumping speed; (*iv*) to increase the pumping speed, the optimum electrode geometry, arrangement and potentials have to be considered in relation to optimum ionization efficiency and maximum ionization current; (*v*) all gases, including the inert rare gases, are cleaned up by electrical pumping; (*vi*) the gas is transported to the positive ion collector electrode and to the walls of a gauge with a glass envelope; in the hot-cathode gauge, transport to the walls is the more important; (*vii*) the gas is retained at the collector electrode and on the walls by surface forces; after a complete monolayer has formed on these surfaces, desorption increases and the gauge pumping action falls off considerably; (*viii*) in view of (*vii*) the effective use of a hot-cathode ionization gauge as a pump is best at initial pressures below 10^{-7} torr; (*ix*) the gas ions reaching a charged collector electrode will penetrate more deeply, the higher their incident energies, *i.e.* the greater the negative potential on the electrode, leading to more effective retention of the gas at this electrode.

The Bayard–Alpert type of hot-cathode ionization gauge has been that most used as a pump, firstly, because it is able to record the low pressures obtainable (down to 10^{-11} torr) and, secondly, because the retention of the gas at the glass walls is a predominant factor in view of the fact that, as compared with the conventional gauge design (§ 3.9), these walls are not screened from the ionization region.

This type of gauge has been widely used in the production of ultra-high vacua in small vessels (Chapter 8) and is also employed in the reduction of the pressure in some specialized types of radio valves during ageing. For example, a transmitter valve may have an ionization gauge attached by a side-tube with a constriction; after the valve has been pumped and processed it is sealed off from the diffusion pump with the ionization gauge still in position. As the transmitter valve is subsequently run on an 'ageing' rack, the continuous operation of the ionization gauge serves not only to monitor the pressure but also to remove gas desorbed from the valve electrodes. Though the pumping speed of this ionization gauge is small, this is not important, as the ageing process may continue for several hours or even days. Eventually the ionization gauge is sealed off from the valve at the pre-heated constriction. This gauge may then be used again provided it is first degassed thoroughly. A small getter-ion pump of the titanium or zirconium type (§ 7.6) may be used as an alternative to the ionization gauge, but this would usually be discarded after use; as the cost is only a few pounds compared with that of the expensive transmitter valve, the procedure is economically satisfactory.

A Bayard–Alpert gauge operated with an electron current of 10 mA, grid potential of 150 V, ion collector potential of −20 V and a sensitivity of 20 μA per mA at 10^{-3} torr will provide a pumping speed of as much as 0·1 litre per sec at a pressure of 10^{-7} torr.

Comsa and Musa (CM1) have proposed an even simpler and yet more effective construction of an ion-sorption pump than the Bayard–Alpert gauge which, however, has the disadvantage that it is unable to record gas pressures. Recognizing that the main pumping action is to the glass walls of the gauge, they dispense with the central ion collector wire electrode used in the Bayard–Alpert design. Their pump consequently has only two electrodes; the dimensions employed are given in Fig. 7.3. With 300 V between grid and filament, almost all ions which reach the glass wall do so with energies between 100 and 250 eV. A rigorous degassing of this pump is an essential preliminary. With an electron current of 10 mA and a grid voltage of 200 V, the measured pumping speed for air was 0·18–0·2 litre per sec which increased to 0·25 to 0·27 litre per sec on raising the grid potential to 300 V. These speeds were found to be practically independent of pressure over the range between 10^{-5} and 10^{-8} torr.

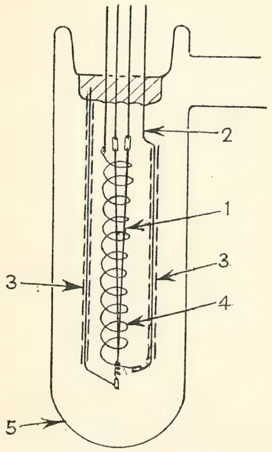


FIG. 7.3 Ion-sorption pump due to Comsa and Musa

(1) tungsten filament, dia 0·1 mm; (2) molybdenum lead-in wire, dia 1 mm; (3) glass sleeves; (4) grid, dia 10 mm wound from 0·2 mm dia tungsten wire; (5) glass wall, 50 mm dia

Houston (H17) has designed an ultra-high vacuum gauge of the hot-cathode ionization type in which combined electric and magnetic fields ensure very long electron trajectories and hence high ionization of the residual gas at very low pressures in the range from 10^{-8} to 2×10^{-12} torr. This gauge can be used as an ion-sorption pump to produce ultra-high vacua with a higher pumping speed than the Bayard–Alpert pattern.

Ionization of the gas in a cold-cathode discharge is utilized in a design of ion pump due to Gurewitsch and Westendorp (GW2). Two circular carbon plates (each 1 in. dia and $\frac{1}{16}$ in. thick) are mounted parallel to one another at a separation of $\frac{3}{4}$ in. (Fig. 7.4). Between these plates is mounted a 1 in. dia molybdenum ring electrode supported by a lead to a glass insulator. The envelope of the pump is a cylindrical box of stainless steel. A horseshoe magnet with additional cylindrical pole-pieces provides a magnetic flux density of about 1000 gauss with the lines of magnetic force perpendicular to the carbon plates. The arrangement is therefore similar to a Penning gauge (§ 3.10). This pump is connected by a tube to the volume to be evacuated. The p.d. across the ring electrode as anode and the electrically connected carbon plates as cathode is 1000 to 10,000 V. As in the Penning gauge, the electrons perform many oscillations about the anode plane before they are collected, producing considerable ionization in the process. The positive ions are driven into the surfaces of the negative carbon plates as a result of their acceleration in the electric field. Secondary electrons and photoelectrons (photons are produced in the excited gas) enhance the ionization.

This pump was operated at pressures from 10^{-1} down to 5×10^{-7} torr. It is reported that 0·07 litre of air at S.T.P. could be absorbed in this pump without saturation effects occurring. A similar pump using titanium cathodes instead of carbon was able to reduce the pressure of hydrogen in a 3 litre vessel from 5×10^{-2} to 2×10^{-4} torr in 9 min approx with an alternating potential (the device is self-rectifying) of 5000 V r.m.s. (open circuit voltage) across the electrodes.

Carbon was presumably used because of its large effective gas-absorbing surface; this material would, however, require prolonged degassing before the pumps were used. The use of titanium—which was suggested—would again demand considerable degassing as a preliminary because of its high hydrogen content. Jepsen (J8) has undertaken an extensive programme of development work on the cold-cathode type of ion-sorption pump with titanium cathodes. His so-called 'VacIon' pump (*Varian Associates Ltd.*) has a pumping speed for air of about 2 litre per sec for a single cell unit (Fig. 7.5(*a*)). The effects of variations of the cathode–anode p.d. and of the magnetic flux density are shown in Fig. 7.5(*b*). It is alleged that, in these pumps, the gas is not sorbed at the cathode but is gettered by the titanium, which is sputtered on to the anode. In this respect, the VacIon pump is a getter-ion and not an ion-sorption type. A multi-cell VacIon pump with a speed of 250 litre per sec (Fig. 7.5(*c*)) and also other models with speeds as high as

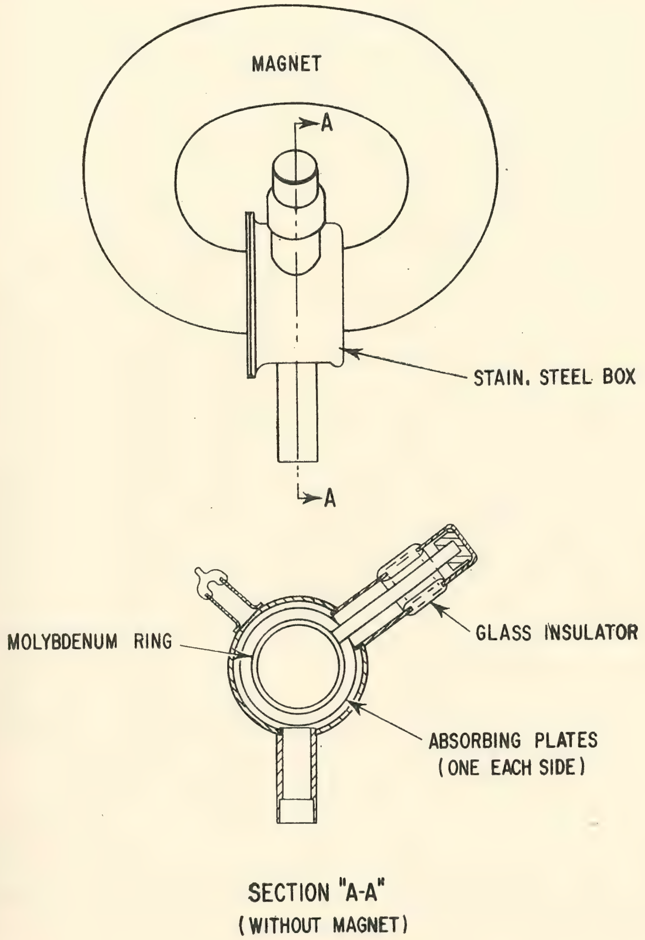


FIG. 7.4 Ion-sorption pump utilizing a cold-cathode discharge due to Gurewitsch and Westendorp

5,000 litre per sec are available commercially. The 'dry' vacuum system designed by Jepsen is shown in Fig. 7.5(*d*). It consists of a VacIon pump backed by a charcoal sorber refrigerated by liquid nitrogen.

Surprisingly little work has been reported on the optimum dimensions and electrical operation of ion-sorption pumps based on the hot-cathode or cold-cathode ionization gauge from the points of view of arriving at the most satisfactory arrangement of electrodes (probably best unlike that in the Bayard–Alpert gauge), the maximum efficiency of production of positive ions, and the effective transport of these ions to surfaces where they will be retained with minimum desorption. Adam (A11) has, however, considered the problem of optimum ion production from the theoretical aspect and has put forward a suggested design of pump for cleaning up gas electrically.

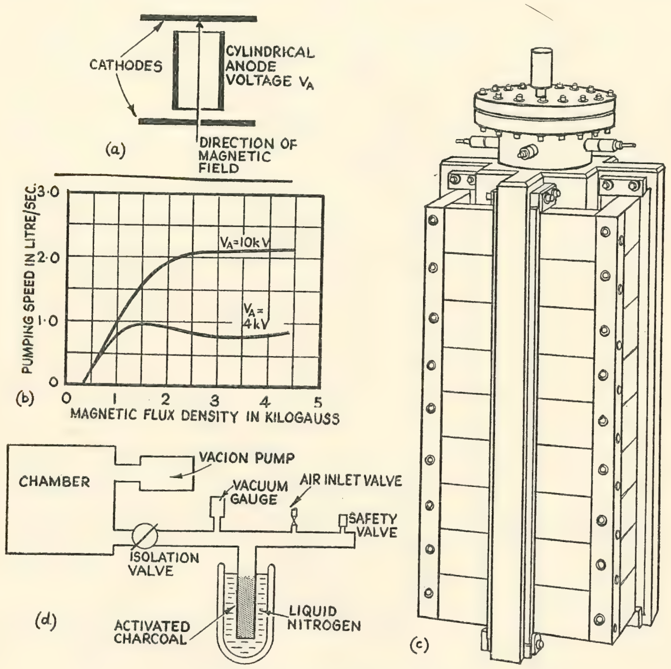


FIG. 7.5 VacIon pumps

A question about which there seems to be considerable differences of opinion is that of the retentions of the ions at the collector or glass wall in these types of ion-sorption pump. The work of Brown and Leck (§ 6.15) shows that, in a Penning–Nienhuis gauge, the positive ions which reach the cathode are neutralized and retained even after the electrode supply voltage is switched off and, furthermore, that this gas is only released by subsequent heating of the cathodes or by subjecting these electrodes to ionic bombardment. In using the Bayard–Alpert gauge as a pump, it is, nevertheless, common experience to find that the sorbed gas begins to re-evolve as soon as the grid accelerating potential is reduced to zero. Incomplete experimental evidence indicates that this desorption is at a small rate if the gauge is thoroughly

degassed at an initial pressure of 5×10^{-8} torr or less before ion pumping is commenced, and, further, that it is less, the larger the effective negative collector potential. In this latter connection, the effective glass wall potential is important as the wall is the chief gas sorber. If the grid potential is at, say, 150 V, the glass wall potential will usually be about zero, so the arriving positive ions will have energies in the range from about 50 to 150 eV, depending on the region of the ionized gas from which they originate. Depending on the electrode geometry, however, it may happen that the glass wall becomes positively charged because electrons that arrive at it with energies in excess of 40 eV can produce more secondaries than primaries (*see* Carter and Leck, CL1).

An advantage of ion pumping as compared with the use of getters is that the rare inert gases are cleaned up, though the exact mechanism in the case of helium is still a topic under investigation (*see* Varnerin and Carmichael, VC1, VC2, and Trendelenburg and Carmichael, TC2).

Getter-Ion Pumps

7.4. Introduction

As the term implies, in the getter-ion pump the highly effective sorption action of getters both during evaporation (dispersal gettering) and in the form of a fresh film on a surface (contact gettering) is utilized and, in addition, the gas is ionized to ensure transport by electrical pumping of the inert rare gases (which are not gettered) to the getter-coated wall at which they are made to arrive with energies of a few hundred electron-volts. At these energies, about a fifth of the ions (which become neutralized) are retained and, furthermore, are eventually embedded in the film as fresh getter is vaporized. The most widely employed getter in these pumps is titanium (§ 6.13). This metal is heated to about 2000° C in a pre-evacuated tube. It volatilizes to form a film on the cool inner walls of the tube. Zirconium has been used in place of titanium. Barium getter-ion pumps have also been constructed, but suffer the disadvantage that the barium metal film must never be exposed to air at pressures in excess of about 10^{-3} torr. Other metals have been proposed but not used to any extent.

Four main types of getter-ion pump are employed in current vacuum practice. First, the large metal pumps in which titanium is evaporated from a continuous feed device and having pumping speeds of a few thousand litres per second, the pioneer work being due to Herb and his colleagues (HDDS1) at the University of Wisconsin, U.S.A.; this type of pump is marketed in U.S.A. by the Consolidated Electrodynamics Corporation and is known as the CEC Evapor-ion pump. Second, small pumps with speeds of about 5 litre per sec in which the titanium is evaporated from a heated tungsten filament loaded with this metal and where a hot-cathode ionization source is used. Third, similar pumps, usually of greater speeds, in which a cold-cathode ionization source is employed, *i.e.* a Penning type gauge. Fourth, the getter-ion pump in which barium is evaporated, which has not been made commercially and is still in the prototype stage.

All these pumps have to operate relative to a fore-vacuum, best at a considerably lower pressure than that necessary for a diffusion pump. The chief object of the large metal designs is to provide high pumping speeds at low pressures (10^{-5} to 10^{-7} torr) without the back-streaming difficulties associated with the use of vapour pumps and without the necessity for a cold trap; the small glass models, on the other hand, are normally used for producing ultra-high vacua (pressures $< 10^{-7}$ torr).

7.5. Large Getter-ion Pumps with Titanium Feed Devices

An improved version of the original Herb pump (HDDS1) is described by Davis and Divatia (DD1). The main pumping chamber is a 12 in. dia stainless steel cylinder 24 in. high. All demountable joints are made with copper or aluminium gaskets to enable bake-out to be undertaken when desired. To evaporate titanium in quantity, a wire of this metal is fed down on to a graphite post *P* (Fig. 7.6(*a*)) which is heated to about 2000° C by bombardment with electrons from the surrounding heated tungsten spiral filament *F*; the post *P* is at 1000 V whilst the filament is at 100 V, both with respect to the earthed cylindrical metal pump chamber. The tungsten filament is operated at 12 V, 25 amp, the current to the post then being 500 mA. The titanium wire (0·02 in. dia) is on a spool *O* mounted in a chamber sealed to the top of the main 24 in. stainless steel tube by the copper gasket *S*. To feed this titanium wire end continuously against the heated carbon post, the feeder mechanism *R*, shown in Fig. 7.6(*b*), is used. Motion must be imparted to this mechanism from outside the vacuum pump via a vacuum-tight seal. To ensure a satisfactory seal without the use of grease or rubber, a thin-walled flexible Kovar tube ($\frac{1}{4}$ in. o.d.; 0·010 in. wall thickness) is copper-brazed at *Z* to the shoulder at the bottom of the cylindrical hole in the feeder block *B*. This feeder block enters the pump wall from which it is electrically insulated by the ceramic rings I_1, I_2, with vacuum seals as shown in the diagram. A wobble stick *W*, within the Kovar tube, is pivoted at *P* and connected at its end to a driver plug *D*. The left-hand end (as in the diagram, in practice the feeder will be inserted perpendicularly into the vertical pump wall) of the wobble stick, which is outside the vacuum system, is moved eccentrically by the driving shaft *M* which is connected to a variable speed electric motor. The titanium wire from the spool inside the vacuum pump is gripped between the driver plug *D* and the leaf *L* during part of the motion and is pushed forward about $\frac{1}{16}$ in. (*see also*, Fig. 7.6(*c*)). As the driver plug rotates further, it moves away from the wire, so relaxing the grip; simultaneously, the locking arm *A*—which is clear of the wire during its movement—is arranged to press on the wire to prevent slip. The leafs C_1, C_2 and C_3 ensure that the driver plug traverses a rectangular path. The wire is seen to be fed in a series of intermittent but regular spaced motions down on to the heated graphite post. The rate of feed of the wire could be varied (by altering the speed of the motor drive) from 0·4 mm to 19 mm of wire per min, corresponding to 0·35 mg per min and 17 mg per min of titanium, respectively.

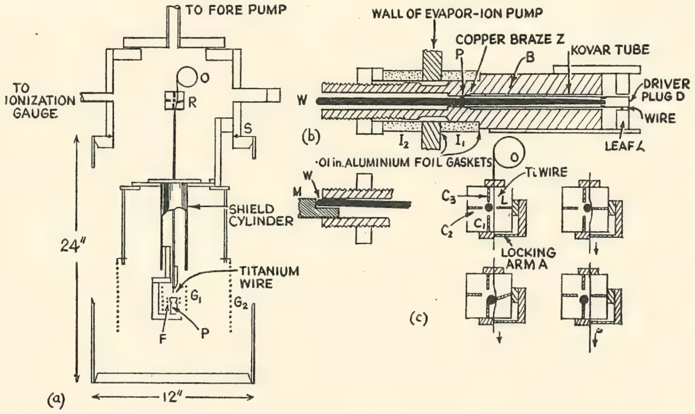


FIG. 7.6 Titanium getter-ion pump (*Davis and Divatia*)

Titanium has a melting point of 1660° C and a vapour pressure of 10^{-1} torr at 1742° C. As it is fed on to the graphite post at 2000° C it therefore volatilizes rapidly (the getter-ion pump being pre-evacuated) and forms a fresh film on the inner surfaces of the pump walls. As it exhibits marked chemisorption for hydrogen, oxygen, nitrogen, carbon monoxide and carbon dioxide, and, moreover, the compounds formed are stable solids with low vapour pressure, the pressure in the pump decreases considerably.

To ensure that the gas within the pump is also ionized and that transport of inert gas ions (which are not gettered) takes place to the titanium film on the wall, where many of them are retained, *i.e.* to provide electrical pumping as well as gettering, the tungsten filament *F*, which is used to provide electrons for the heating by bombardment of the graphite post *P*, also provides electrons for ionization of the residual gas molecules on collision. This filament is therefore surrounded by a cylindrical coaxial inner grid G_1 ($1\frac{1}{4}$ in. dia) and a second outer grid G_2 (8 in. dia). With the filament at +100 V with respect to the earthed pump wall and the grids G_1 and G_2 at +1000 V, a grid current (to G_1) of 200 mA is provided. The positive ions are formed mostly within the region between the grids and are driven into the earthed wall (which is coated with the titanium) with maximum energies of 1000 eV (assuming the ions are singly charged). At a pressure of 2×10^{-7} torr, the positive ion current to earth was 10 μA, a figure open to doubt as secondary electrons are released from the wall. Ceramic electrical insulation is used and shields disposed at suitable places to prevent electrical leakage due to deposited titanium.

The sequence of operations recommended by Davis and Divatia in using this pump is as follows:

(*a*) A fore-pump (mechanical rotary) is connected to the part shown at the top of the diagram (Fig. 7.6(*a*)) via a liquid-air trap.

(*b*) The pump chamber below the gasket seal *S* is heated in an oven to about 300° C for about 6 hours. On cooling, a pumping action takes place to produce a pressure of about 10^{-4} torr (no vacuum tank is connected to the getter-ion pump—the experiments described are in relation to pressure readings recorded by the hot-cathode ionization gauge connected via a small side-tube near the top of the pump).

(*c*) The fore-pump with cold-trap is isolated by a vacuum valve from the getter-ion pump and the evaporation of titanium is begun.

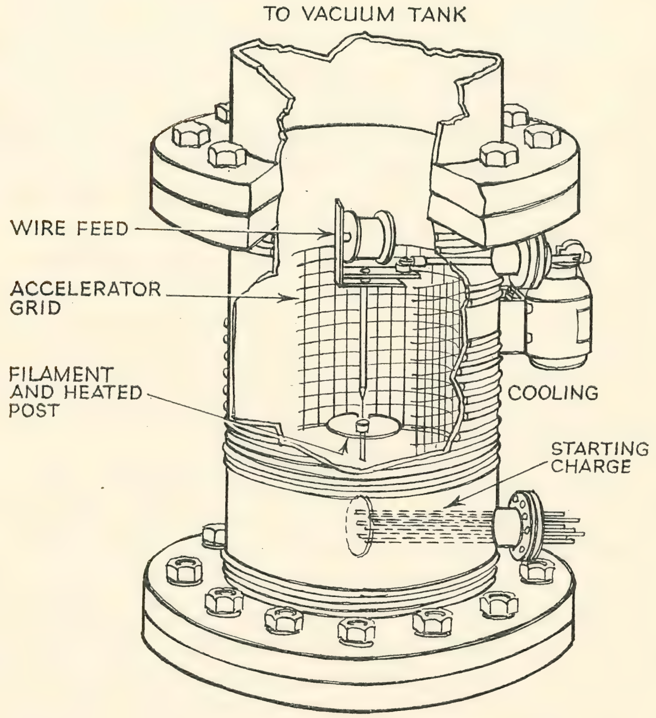


FIG. 7.7 The evapor-ion pump (*Consolidated Electrodynamics Corporation Model No. 3161-01*)

With the pump walls at a temperature of 20° C approx, the pumping speeds in litre per sec recorded by the constant pressure method were 7000 to 8000 at 3×10^{-6} torr for H_2, 6500 to 7500 at $1{\cdot}5 \times 10^{-6}$ torr for nitrogen, the same for oxygen, 1000 at $1{\cdot}5 \times 10^{-6}$ torr for air, 9 at 4×10^{-6} torr for argon and 4 at 3×10^{-5} for argon.

Swartz (S22) gives details of the performance of the getter-ion (evapor-ion) pump made by the Consolidated Electrodynamics Corporation (*see* this firm's bulletin No. 6140-Z-3). This pump is based on the model designed by Davis and Divatia described in the foregoing. A sketch (Fig. 7.7) shows that the vacuum tank to be exhausted is connected to the top of the getter-ion pump whilst the fore-pump is joined through an isolation valve either to the base of the getter-ion pump or via a side-tube. The dimensions are similar to those of the pump shown in Fig. 7.6. In this pump, the heated post (electron bombardment heating is used) at which the titanium wire melts and vaporizes is made of tantalum–tungsten alloy instead of graphite, as the latter tends to cause titanium carbide to be formed and is liable to disintegrate. The feed device utilizes sylphon bellows instead of a thin-walled Kovar tube. A net-like grid maintained at +1000 V accelerates electrons from the tungsten filament around the post. These electrons ionize the residual gas and these gas ions are, as before, driven into the titanium-coated wall. The pump walls are water-cooled by means of the surrounding spiral shown in the diagram (*see also* Plate 5).

Swartz points out that the use of voltages of the order of 1000 between the post and the filament and also the grid and the filament would lead to a glow discharge if the pressure were greater than 3×10^{-4} torr approx. To ensure sufficiently low initial pressures in the pump, the pressure of about 10^{-2} torr created by the rotary fore-pump (the 10^{-4} torr attained by Davis and Divatia was only after heating and cooling) is decreased to about 10^{-4} torr by the evaporation of an auxiliary charge of titanium from one of the six tungsten filaments in the pump near the base. The filament is heated by the direct passage of electric current. The evaporation is performed after the isolation valve to the rotary fore-pump has been closed but before the main titanium evaporation from the wire feed to the heated post is started.

Speeds at constant pressure recorded for this pump by Swartz were 50 to 85% less than those quoted by Davis and Divatia, probably because of the difference of arrangement of the gas leak in the two experiments. The figures given by Swartz are more realistic, as it was ensured that the leaked-in gas was first directed against a baffle in the test-dome before diffusing into the pump. Swartz's results for the pumping speeds in litre per sec were: hydrogen, 3300 at $1{\cdot}7 \times 10^{-6}$ torr; nitrogen, 2000 at 3×10^{-6} torr; oxygen, 1000 at 10^{-5} torr; carbon monoxide, 1000 at 5×10^{-6} torr; air, 370 at 10^{-5} torr; methane, 20 at 10^{-5} torr; argon, 5 at 5×10^{-5} torr. The titanium was evaporated at the rate of 5·3 mg/min.

If the pump has been opened to the atmosphere for some hours, the fore-pump started and some of the auxiliary titanium charge evaporated to give a pressure of about 10^{-4} torr, then, according to the pump-down curve given by Swartz, 1 hour after the getter-ion pump proper has been started, the pressure decreases to about 5×10^{-6} torr, after 10 hours it is about 7×10^{-7} torr, and nearly 10^{-7} torr is attained after 100 hours. Baking the getter-ion pump to about 300° C during the fore-pump operation reduces this subsequent pump-down time considerably. On the other hand, with a thoroughly degassed pump initially at 4×10^{-7} torr, argon (the most abundant of the rare gases in the atmosphere) admitted to a pressure of about 4×10^{-5} torr could be removed to give a pressure of about 10^{-6} torr in 100 sec with a titanium feed-rate of 5 mg/min.

Swartz's mass spectrometer analysis of the residual gases in this pump at a pressure of 2×10^{-6} torr show prominent peaks for hydrogen, water vapour, nitrogen, argon and carbon dioxide and also subsidiary peaks corresponding to organic contaminants. Despite the affinity of titanium for hydrogen (§ 6.13) this gas is often the prevalent constituent during the first hour of pumping after exposure to the atmosphere; subsequently, water vapour predominates. Water vapour is alleged to be removed chiefly by ion pumping rather than gettering—which seems surprising. Baking the pump casing to between 50° and 100° C after the fore-vacuum is established (isolation valve closed) reduces organic contaminants but does not appreciably speed up the rate of removal of hydrogen, nitrogen, argon and water vapour.

Satisfactory maintenance-free life-times of at least 1000 hours for these pumps are recorded, though the component most likely to fail early is the titanium feed-device due to build-up of titanium on the tip of the guide tube, and difficulty is also experienced due to peeling of the titanium film on the pump walls after repeated evaporations, especially if air at atmospheric pressures is frequently admitted. According to Adam (A18), the life of a medium-size getter-ion pump (several hundred litre per sec for N_2) is about 1700 hours of operation time between rechargings with titanium wire.

To reduce the difficulties associated with raising to high temperature the end of the titanium wire fed against the post, Holland (H18) has proposed that this end is fed directly into an electron beam. Experiment showed that a molten globule of titanium could be obtained on the end of a wire fed downward, but that this globule then retracted under surface tension forces from the electron beam; sufficiently high temperatures were not obtained, therefore, for rapid evaporation. A development from this idea has, however, been used in a design of titanium getter-ion pump described by Holland, Laurenson and Holden (HLH1). The titanium wire is fed downwards against the inclined face of a water-cooled copper block (Fig. 7.8). The end of the wire is then at the same potential as the copper block, which is made positive with respect to a heated tungsten filament that emits electrons. A hemispherical globule is formed on the free end of the wire as a consequence of the heat generated on electron bombardment and this globule hangs from a frozen zone adhering to the cooled copper. If the globule becomes detached from the titanium wire, it remains suspended from the copper. Hot spheres of titanium at a temperature of 2000° C and of up to 5 mm radius have been produced in this way. The use of the inclined plane on the copper block prevents the exit of the guide tube from becoming blocked by titanium melting back. If the wire feed does become obstructed due to the wire sticking to the copper, this does not matter as the wire simply bends sideways and continues to enter the beam to form another globule. According to Holland *et al.* the life-time of this type of source is limited only by that of the thermionic filament which tends to become eroded by positive ion bombardment.

With this feed device within a water-cooled 18 in. dia getter-ion pump and titanium wire of 0·04 in. dia, evaporation rates of 250 mg/min max were achieved with a power input of 6 kW. With an evaporation rate of 100 mg/min (anode-filament p.d. of 1 kV and electron current of 1·2 amp) pumping speeds achieved for air were about 1000 litre per sec at 10^{-5} torr.

Holland *et al.* point out that, in the Herb type of pump (*cf.* the Davis and Divatia version in Fig. 7.6), if the pressure is more than 10^{-4} torr and the thermionic filament is earthed, ions produced within the filament-grid space will bombard an earthed wall and may remove absorbed gas from the condensed titanium deposit rather than be trapped themselves. They therefore insulate the filament heater transformer from earth at the higher gas pressures. A pumping procedure recommended by these workers is: (*i*) reduce the pressure within the getter-ion pump to about 5×10^{-4} torr by means of a two-stage rotary pump, (*ii*) operate an auxiliary thermionic filament and degas the pump walls by electron bombardment (walls positive w.r.t. this filament), (*iii*) evaporate titanium to reduce the pressure by gettering to about 10^{-5} torr, (*iv*) apply the appropriate potentials to the filament and grid with the walls earthed to initiate ion pumping. The ultimate pressure recorded was 10^{-6} torr.

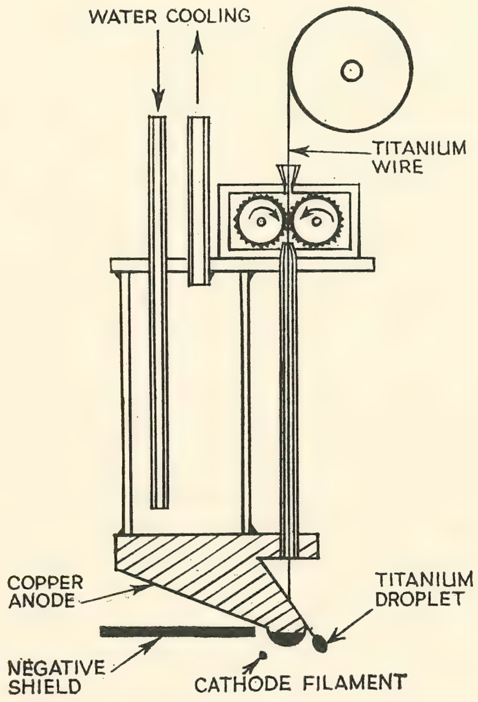


FIG. 7.8 Titanium evaporation source for a getter-ion pump (*Holland, Laurenson and Holden*)

As argon forms about 1% of air at atmospheric pressure and the pumping speed at 10^{-6} torr of a 12 in. dia titanium getter-ion pump is only about 5 litre per sec for argon as compared with 2000 for nitrogen—because argon is only removed by ion pumping and not by the gettering action alone—it is important to consider the optimum design of the filament and grids used to produce the ionizing electrons in these pumps. This topic has been the subject of a design of experimental getter-ion pump introduced by Alexeff and Peterson (AP1). They showed by measurement that the sticking probabilities (ratio of number of gas atoms trapped to the number of ions incident on a target) for argon on a titanium-coated (fresh deposit) pump wall are 0·22 for an incident positive ion energy of 600 eV, 0·2 for 500 eV, 0·16 for 400 eV and 0·12 for 350 eV. As these ratios are satisfactory, *i.e.* trapping within titanium is efficient, the design problem is reduced to the attainment of efficient ionization of the gas.

This efficiency of ionization was increased considerably by the use of a system of a thermionic filament and two grids which had high transparency to ensure that the electrons executed long oscillatory paths about the grid wires before collection. Furthermore, parts of the titanium evaporator and other components which might absorb electrons prematurely were either electrically shielded from the ionization region or reduced in size as far as practicable. An axial magnetic field was used to increase further the electron paths by causing them to spiral. With the two grids both at +500 V with respect to the thermionic filament (separate from the evaporator filament) and this filament at +250 V with respect to the earthed wall, the positive ions were driven into the titanium-coated wall under the action of a potential difference of 750 V. For a total grid current of 1 amp, the speed of pumping for argon was 250 litre per sec, and effectively constant over the pressure range from $2{\cdot}5 \times 10^{-6}$ to 2×10^{-5} torr. For helium, the speed was 90 litre per sec at 2×10^{-5} torr.

To ensure sufficiently low initial pressures before volatilizing the titanium, but without the use of auxiliary titanium-charged filaments, a Roots pump (§ 2.7) is often employed in series between a conventional rotary fore-pump and the large getter-ion pump. This arrangement leads, however, to a very expensive set-up and also an elaborate one in view of the additional requirement for power-packs of considerable size for the electrical operation of the getter-ion pump. Water cooling of the larger getter-ion pump walls is also essential to avoid re-evolution of the gases sorbed by the titanium coating. Safety devices to protect against failure or partial failure of a refrigerated trap (not used) and water cooling are, however, not so elaborate as those demanded with large oil vapour and mercury vapour pumps.

Holland (H16) reports that, on vaporizing 300 mg of titanium per minute in an 18 in. dia pump, the pumping speed passed through a maximum and then decreased as the deposited film became heated by radiation from the vapour source. He suggests that this fall-off is a result of the gas content of the titanium film increasing on pumping, which will cause a decrease of thermal conductivity so that heat is not conveyed away so rapidly from the exposed surface of the film to the cooled walls.

The large titanium getter-ion pump has already been applied to a considerable extent in those cases where a high pumping speed coupled with 'dry' (*i.e.* oil vapour free) residual gases at low pressure (10^{-6} to 10^{-7} torr) are required in chambers of considerable size. Equipments in which these pumps have been used with advantage are high energy particle accelerators (*e.g.* Van de Graaff generator, microwave linear accelerators, proton-synchrotrons) and large demountable X-ray tubes and betatron X-ray tubes.

Gould (G15) proposes to install about 50 large getter-ion pumps in the vacuum system of the 30 BeV (30×10^9 eV) proton-synchrotron which is under construction at the Brookhaven National Laboratory, New York, U.S.A.

There is little doubt that these pumps will find increasing application as their design is improved and as the demands on vacuum technology increase. Reports of the attainment of ultimate pressures by the pumps of 10^{-7} and even as low as 10^{-8} torr occur in the literature; it is doubtful, however, whether ultimates much less than 10^{-6} torr can be consistently achieved with long periods of operation under conditions where air is repeatedly admitted to the pump unless considerable maintenance (*e.g.* cleaning-off of wall films) is undertaken. For this reason it is usual practice to attempt to arrange pumping schedules in which the pump interior is seldom at pressures exceeding 10^{-3} torr.

7.6. Small Getter-ion Pumps with Hot-cathode Ionization Sources

A convenient and useful getter-ion pump is that based on the Bayard–Alpert gauge (§ 3.9) in which an extra tungsten filament has wrapped around it a titanium or zirconium wire (*e.g.* a pump of this type is supplied by Mullard Ltd.). Usually, these pumps are first evacuated to diffusion pump pressures (10^{-6} torr or less), but considerably higher initial pressures may be used. On firing the titanium getter, sorption of the common gases takes place; on operating the ionization gauge, positive ions of the gas, and, in particular, the inert rare gases, are driven into the titanium-coated walls where 10 to 20% of those incident are retained and, furthermore, buried in any subsequently deposited titanium. A pumping speed of about 5 litre per sec for air is possible and ultimate pressures of 10^{-9} tor orr less are attainable. A typical application is the improvement of the residual vacuum in a specialized type of thermionic vacuum tube such as an u.h.f tube or transmitter valve; an auxiliary small getter-ion pump in a glass bulb is attached to the main tube. After sealing off the main tube from the conventional pumping system at a pressure of about 10^{-6} torr, the titanium getter-ion pump can be operated to reduce the total residual gas pressure to 10^{-9} torr and this auxiliary pump sealed off at a pre-heated constriction. In production, the comparatively cheap getter-ion pump is then discarded.

The small Leybold getter-ion pump is shown in Fig. 7.9(*a*) and the pump-down curve from 10^{-3} to 2×10^{-7} torr for air on evacuating a container of volume 4·5 litre by this pump is shown in Fig. 7.9(*b*). This curve was obtained after a single short-period volatilization of the titanium, and the ultimate pressure achieved remained constant for a long time. A recommended procedure to obtain an ultimate pressure of about 10^{-7} torr is to pump the vacuum chamber down to pressures less than 10^{-3} torr by a two-stage rotary pump (preferably of the gas-ballast type) first, then to close the isolation valve in the connection to this pump or, if possible, to seal off the chamber—with getter-ion pump attached—by glass-blowing. If this isolation is not undertaken, oil vapour from the rotary pump will enter the chamber continuously.

The titanium in the getter-ion pump is then evaporated and the ionization mechanism switched on. Depending on the size of the vacuum chamber and its outgassing, the pressure will decrease to less than 10^{-6} torr in 30 min to 1 hour. The titanium can be evaporated in two or more stages if required. It does not necessarily follow that a more rapid evaporation of the titanium will cause the pressure to decrease more quickly as the extra heating required may cause additional gas evolution in the chamber.

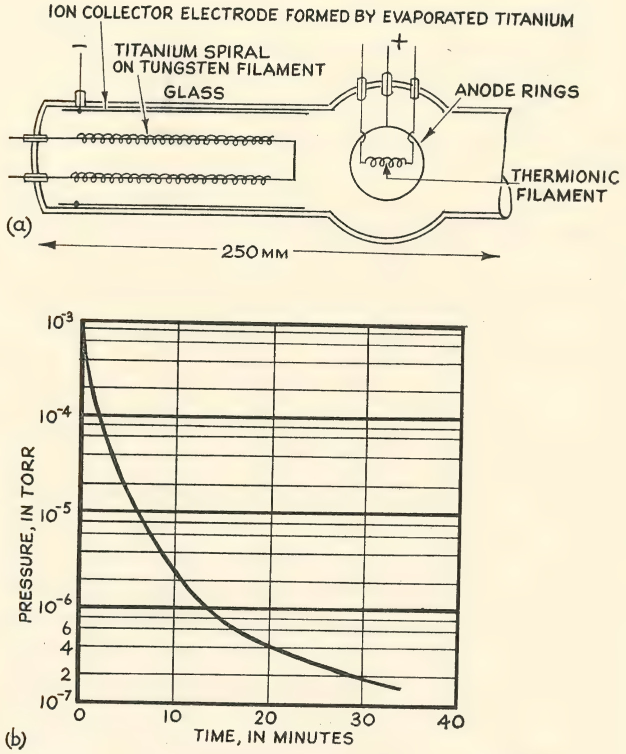


FIG. 7.9 Titanium getter-ion pump (*Leybold*)

The use of these pumps to attain pressures of 10^{-9} torr or less is described in the chapter on ultra-high vacuum technology (§ 8.4).

The electrical characteristics of this pump are:

titanium-charged heater: 4 V, 20 amp max variable voltage source required.
thermionic filament: 5 V, 4 amp max; variable voltage source required.
anode voltage: 2000 V r.m.s. a.c. or 1500 V d.c.
anode current: 1 to 3 mA.

Using this pump, Reich and Nöller (RN1) analysed the residual gas constituents by means of an omegatron (§ 3.13). The pump, omegatron and an ionization gauge were first evacuated to 10^{-2} torr by a rotary pump and then sealed off. Operation of the getter-ion pump then reduced the pressure to 5×10^{-7} torr after several hours (Note: the initial pressure is 10 times that used in obtaining the curve of Fig. 7.9(*b*)). If the ionizing discharge in both the pump and the ionization gauge were switched off, the pressure increased gradually to reach 2×10^{-5} torr in 16 hours. At this pressure, the mass spectrum obtained established the presence of methane, ethane and, occasionally, propane, but a comparatively small abundance of water vapour, carbon monoxide, argon and helium. It is presumed by these authors that the presence of hydrocarbons is due to the reactions of gases containing hydrogen or carbon with the titanium film. If the ionizing discharge were then switched on again, the pressure decreased to as low as 5×10^{-9} torr after several hours, in the most favourable case, and helium, argon and methane contributed about equally to the residual pressure. The methane partial pressure increased yet again, however, on switching off the ionizing discharge. Hence, if pressures below 10^{-7} torr are to be reliably produced by titanium getter-ion pumps, the system must be first evacuated to about 10^{-6} torr by a diffusion pump and a thorough degassing of the envelope and gauge electrodes undertaken.

Huber and Warnecke (HW3, *see also* Holland, H16) report on the use of a small titanium getter-ion pump to evacuate a klystron tube.

7.7. Getter-ion Pumps with Cold-cathode Ionization Sources

An ion pump with an ionizing discharge created within a Penning type cold-cathode gauge has been described in § 7.3, but this is not a getter pump. Gale (G16) describes a true getter-ion pump utilizing a Penning gauge with a metal envelope which he employed to evacuate a million-volt X-ray tube in which the insulating section comprised a multiple sandwich of insulators and electrodes sealed together by a thermosetting resin (Araldite). As such a structure evolves gas, the purpose of the getter-ion pump was to absorb this gas to prevent rise of pressure in the tube during its life. This pump consisted of a commercial Penning cold-cathode ionization gauge together with one or more tungsten filaments over which was wound titanium wire. This type of pump was used either as an appendage to the X-ray tube or was arranged within this tube. Pumping was carried out first by a mechanical rotary pump to about 10^{-3} torr and the X-ray tube was then sealed off before the titanium was evaporated and the ionizing discharge switched on when the pressure decreased to less than 10^{-6} torr. It is preferable, however, to use two titanium getter-ion pumps, one to assist the rotary pump during initial outgassing and the second after seal-off.

Turnbull (T2) gives details of a getter-ion pump in which the ionization source is a large Penning gauge having a cathode in the form of a 9 in. dia ring of 1 mm dia tungsten wire and a surrounding pill-box shaped anode with a central hole in the top and bottom faces constructed of copper–nickel alloy (Fig. 7.10). These electrodes are within a copper pill-box shape envelope (12 in. dia; 2 in. deep) set between the pole-gaps of a circular array of six permanent magnets. Seals required are by indium gaskets. The titanium is evaporated from the cathode, titanium wire being wound around the tungsten wire ring which is heated by direct passage of electric current to about 1500° C. For nitrogen, the pumping speed was 100 litre per sec at 10^{-3} torr and 1600 litre per sec at 5×10^{-6} torr. The pumping action down to pressures of 10^{-5} torr was due chiefly to the getter, subsequent pressure reduction to 10^{-7} torr being due primarily to the ionization. This pump was designed for evacuating expensive high-power radio valves in a sealed-off system.

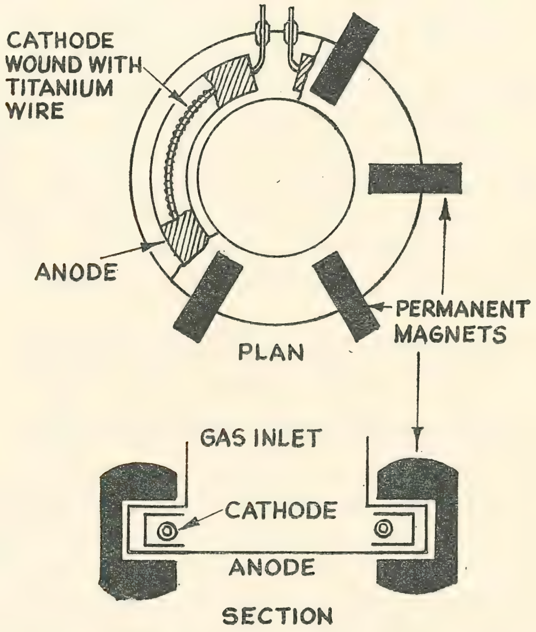

CATHODE WOUND WITH TITANIUM WIRE
ANODE
PLAN
PERMANENT MAGNETS
GAS INLET
CATHODE
ANODE
SECTION

FIG. 7.10 Getter-ion pump with cold-cathode ionization source (*Turnbull*)

7.8. Barium Getter-ion Pumps

As barium getters have outstanding affinity for gases (§ 6.11) their use in getter-ion pumps would afford highly effective removal of gas. As compared with titanium, the chief advantage of barium is that it can be rapidly evaporated *in vacuo* at much lower temperatures (roughly, 800° C as compared with 2000° C) whereas the chief disadvantage is that it deteriorates rapidly on exposure to air. This deterioration involves technical difficulties in the construction yet, despite these, barium pumps have been designed and used, in particular by Cloud, Beckman and Trump (CBT1), whose pump is illustrated Fig. 7.11.

In this barium pump, the barium (which can be purchased in vacuum-sealed cans and, in bulk form, may be exposed to the atmosphere for a day with only slight surface oxidation) is contained in a stainless steel crucible at the base of the main pump cylinder. This crucible is heated by a 1·2 kW electric heater arranged around the outside of the lower part of the pump within considerable thermal lagging. A thermocouple is attached for monitoring the temperature to within 25° C of 800° C. The pump is first evacuated to about 10^{-3} torr by a conventional fore-pump with a cold-trap and the barium evaporated. At 800° C, $\frac{1}{4}$ lb of barium is evaporated in about 45 min. This barium condenses on to the upper part of the pump walls, which are water-cooled, and also on the parallel, stainless-steel fins arranged vertically inside the pump. These fins are spaced sufficiently far apart so as not to prevent the barium vapour from reaching the upper parts of the pump. The isolation valve is necessary to allow air to be admitted to the chamber to be exhausted without exposing the barium. If the barium films are exposed to air, barium oxide formed flakes off (Holland, H16). Using initially a $\frac{1}{4}$ lb chunk of barium metal in the crucible, the pump can be repeatedly reactivated, *i.e.* fresh, active barium films are produced. The Penning gauge attached is used to ensure that the inert rare gases, in particular, argon, are ionized and that large organic molecules are dissociated and excited or ionized so that they are absorbed by the barium.

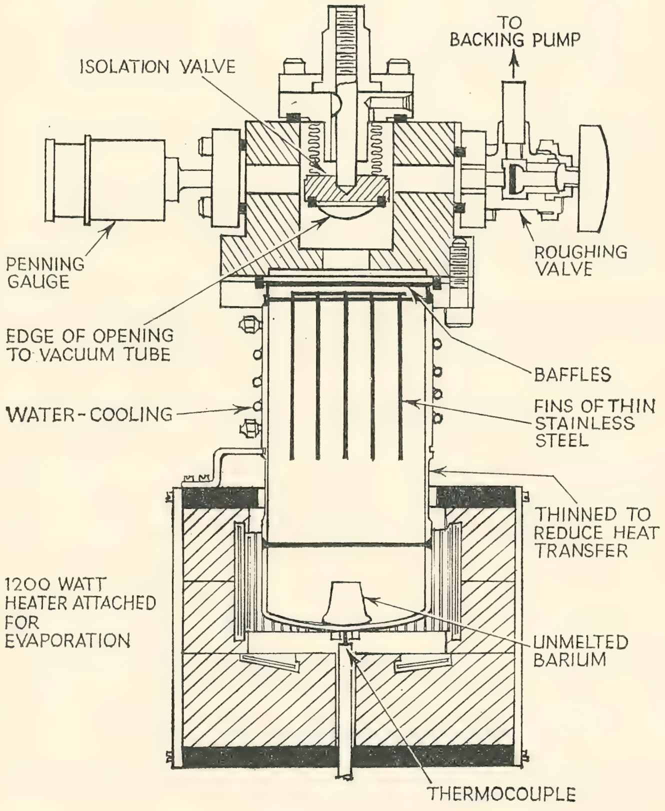

TO BACKING PUMP
ISOLATION VALVE
PENNING GAUGE
ROUGHING VALVE
EDGE OF OPENING TO VACUUM TUBE
BAFFLES
WATER-COOLING
FINS OF THIN STAINLESS STEEL
THINNED TO REDUCE HEAT TRANSFER
1200 WATT HEATER ATTACHED FOR EVAPORATION
UNMELTED BARIUM
THERMOCOUPLE

FIG. 7.11 A barium getter-ion pump (*Cloud, Beckman and Trump*)

Polyethylene or Neoprene gasket seals used in the pump construction were satisfactory.

To clean a barium pump after use, the dismantled pump cylinder with barium crucible removed may be immersed quickly in water (care is necessary as an exothermic reaction is liable to take place which may cause a mild explosion and flame), and subsequently further cleaned and dried thoroughly.

To determine the pumping speeds and capacities for various gases, Cloud, Beckman and Trump removed the valve block from the pump top inlet port and closed this opening by a flat plate sealed with a polyethylene gasket. A Penning gauge, of known calibration for nitrogen and estimated conversion factors for the other gases, was mounted on the top flange. In some experiments, a second specially designed Penning gauge in a cylindrical chamber 3 in. high was mounted between the pump cylinder and its cover plate. This second gauge and its surroundings became coated with a thin barium film during the evaporation.

After deposition of the film, pure gas was admitted through a capillary attached to the top cover plate. The results obtained for various gases are summarized in Table 7.1.

TABLE 7.1

Pumping speeds and half-value capacities[1] for various pure gases[2] admitted to the barium getter-ion pump (Cloud, Beckman and Trump)

Gas	External Penning gauge only		Both external and internal Penning gauges	
	Initial speed, litre/sec	Half-value capacity, litre-torr	Initial speed, litre/sec	Half-value capacity, litre-torr
Air	0·9–1·5	30	6·9	
Argon	0·01		0·2	
Carbon dioxide	50		70–120	
Hydrogen	140		140	500
Nitrogen[3]	10	25	17	45
Oxygen	50–60	650	120–220	

[1] Half-value capacity is defined as quantity of gas (measured here in litre-torr) which reduces the pumping speed to half its initial value.

[2] Tank gases were also used (oxygen, nitrogen, and hydrogen) but were not pumped so readily because they contain small amounts of argon. This is also the reason for the comparatively small pumping speed for air.

[3] Tank gas.

The initial pumping speed was found to be independent of pressure over the range from 5×10^{-6} to 5×10^{-4} torr. The ultimate pressure (no inlet gas) was about 10^{-7} torr.

The very low pumping speed for argon is noteworthy. Also, the presence of this gas in air and in tank nitrogen has an adverse effect on pumping speed. On operating the internal ionization source (*i.e.* the second Penning gauge) the speed for argon is, however, increased 20 times and the speeds for air and nitrogen are enhanced considerably. Moreover, with this internal source in operation, the half-value capacity for tank nitrogen is increased, a result which probably holds also for other gases containing argon.

It was concluded, as had been shown previously by other investigators using titanium getter-ion pumps (§ 7.5), that the noble gases are not absorbed by the barium film unless their molecules are previously ionized. Furthermore, the increase of speed resulting from the use of the internal ionization source as distinct from the use of a Penning gauge attached to a side arm, indicates that the noble gas ions are best produced in the immediate vicinity of the barium film, though some absorption does take place even if the gas is ionized at a comparatively remote location. These considerations also seem to apply to some types of large organic molecules (*e.g.* from polyvinyl acetate and cold-setting epoxy resins) in that they appear to be sorbed by the barium only if the vapour molecules concerned are in an excited or ionized state.

Sibata, Hayashi and Kumayai (SHK1) have described recently a barium getter-ion pump with a cylindrical envelope 40 in. long by 14 in. dia. The barium is distilled from an auxiliary chamber via a thin tube into the heated crucible in the main chamber. An ultimate pressure of 10^{-7} torr is claimed and a pumping speed of 5000 litre per sec for oxygen.

Barium getter-ion pumps have been used for maintaining low pressures in high energy particle accelerators. Indeed, a possible development is the construction of particle accelerators with built-in barium pumps. In effect, such a system is comparable from the vacuum point of view with the small radio receiver valve containing a small getter. Cloud, Beckman and Trump (CBT1) report that a high voltage accelerator tube employing 10 polyethylene and 2 rubber gaskets was maintained at a pressure of between 10^{-7} and 10^{-6} torr by the presence of a barium film which had to be reactivated (*i.e.* fresh barium evaporated) every month.

7.9. Reactivation of Titanium by Abrasion

The capacities for gas of titanium and barium are limited because of the formation of, in particular, oxide films. In the getter-ion pumps, reactivation of the film is accomplished by evaporation of a fresh deposit on top of the old one, as described previously. Haine, Francis and Bloomer (HFB1) suggest that the alternative to a new deposit is to abrade the old one to remove the oxide or other protective skin and expose the fresh surface beneath. To demonstrate that this is effective, they constructed a trough made of sheet titanium in which was placed a few pieces of carborundum or 'some pieces of an old metal file'. Though this conjures up odd ideas about the titanium pump design of the future, it is nonetheless significant that, when this arrangement was mounted in a glass bulb, shaking of the abrasive in the titanium trough did cause a significant fall of gas pressure. In one experiment, the device was evacuated by conventional pumps and baked to leave a residual gas pressure of 10^{-6} torr (as measured by an attached ionization gauge). On admitting gas via a porous ceramic tube to increase the pressure to 10^{-4} torr, shaking to cause abrasion of the titanium surface reduced the pressure to 10^{-6} torr in less than a minute. Moreover, this operation could be repeated several times until so much powdered titanium salt was produced as to reduce considerably the gas sorption.

8

ULTRA-HIGH VACUUM TECHNOLOGY

8.1. Introduction

Though the term 'ultra-high vacuum' is apparently not favoured by the British Standards Institution in that it does not appear in their *Glossary of Terms Used in High Vacuum Technology*, it will be used here to cover those cases in which the pressure in a container is 10^{-7} torr or below. The B.S.I. recommendation is to use the term 'very high vacuum', but the use of the word 'ultra' in this connection has become virtually accepted parlance in recent years. The American Vacuum Society recommendations are different again in that they suggest the use of the term 'very high vacuum' to denote the pressure region from 10^{-7} to 10^{-9} torr, and 'ultra-high vacuum' for 10^{-9} torr and below. This suggestion is sound in that, as will be seen in this text, the techniques for producing pressures of 10^{-9} torr or below are different from, or additions to, those which can produce pressures down to 10^{-9} torr.

In general, the technology demanded for producing pressures less than 10^{-7} torr excludes kinetic systems in which rubber, artificial rubber or plastic (except for P.T.F.E.) components and/or grease are used. Furthermore, though glass and ceramic constructional materials are admissible, the use of mild steel or brass is ruled out though drawn stainless steel and copper may be employed. It is necessary to degas the chamber by bake-out and any internal metallic structure should be degassed by induction-heating or electron bombardment.

The factors which influence the ultimate pressures obtainable by diffusion pumps have been considered in § 2.14. At pressures less than 10^{-6} torr, even the best designed pump is inadmissible unless it has effective means of preventing the pumping fluid from back-streaming into the chamber, as otherwise it becomes a source of contamination of the vacuum rather than an effective means of gas removal.

For mercury diffusion pumps the method of preventing back-streaming is a cold-trap filled with liquid air or liquid nitrogen (§ 2.11). Baffles at room temperature (or water-cooled) are, however, effective with oil diffusion pumps, though again the best results will be obtained with a liquid nitrogen trap.

In the case of small glass systems where the chamber can be readily degassed, pressures of 10^{-7} torr are readily obtained and 5×10^{-8} or even 10^{-8} torr is possible. To ensure the lowest ultimate of about 10^{-8} torr, the glass vessel should be baked for some 4 hours (and preferably overnight) and internal metal parts must be induction-heated or electron-bombarded. Furthermore, any auxiliary glass or glass-to-metal tubing to the system should be baked either in the oven or by wrapped-round thermal tapes. Careful attention must also be paid to the cold-trap design used with mercury diffusion pumps if very low ultimates are to be achieved, as otherwise minute droplets of mercury may collect on upper parts of the trap which are not cooled to liquid air temperature. A useful trap which is somewhat difficult to fabricate but which is very effective is that shown in Fig. 8.1. This consists, in effect, of two bulbs within the tubulation joining the mercury diffusion pump to the chamber. Both these bulbs become filled with liquid air on filling the surrounding double-walled container because each bulb has two openings connecting to this container. Any minute quantities of mercury likely to pass the lower bulb are certain to be trapped at the upper bulb; it is effectively a double cold-trap (*see also* § 8.2). If an oil diffusion pump is used then probably the most effective type of baffle against backstreaming is the copper-foil trap due to Alpert (A12), and shown in Fig. 8.2. It is emphasized that the copper foil must be thoroughly cleaned before use. Alpert reports that this type of trap at room temperature is effective for one or two months and that it can be renovated by baking together with the rest of the vacuum system.

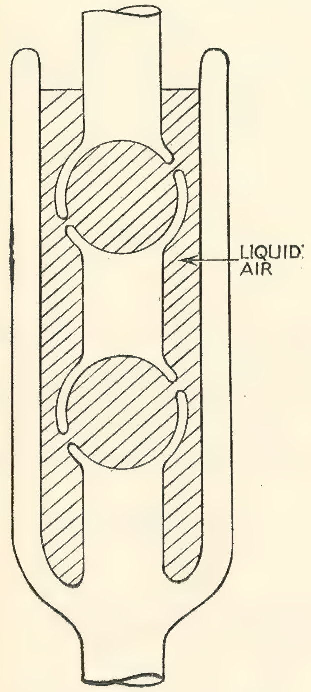


FIG. 8.1 Cold-trap with double bulb

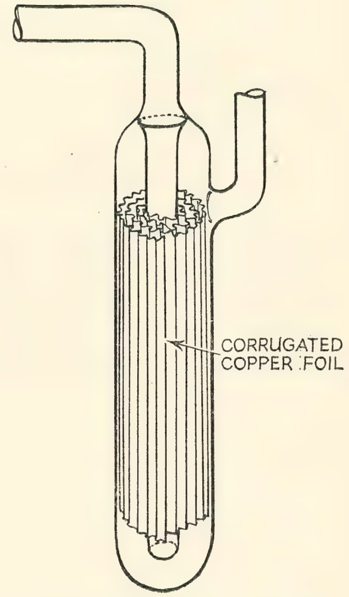


FIG. 8.2 The copper-foil trap (*Alpert*)

As the performance of the system may be vitiated by the migration of oil from the rotary pump into the diffusion pump via the backing line, a water-cooled trap like that shown in Fig. 8.3 is recommended to prevent this. A trap of this kind should be fitted to all types of ultra-high vacuum system which employ a rotary/diffusion pump combination.

Ultimate pressures of 10^{-8} torr can certainly be attained with such glass systems if long term bake-out is practised.

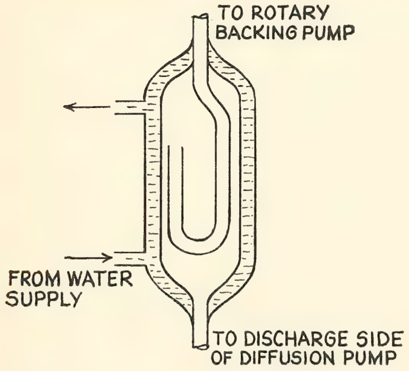


FIG. 8.3 Water-cooled trap to prevent oil vapour from the rotary backing pump reaching the diffusion pump

The problem of attaining low ultimate pressures in large metal systems is not so easily solved; the most probable course of development is by the use of a diffusion pump with a liquid nitrogen trap or the getter-ion pump. Stainless steel chambers which are sealed by hard-soldering, welding or with metal gaskets are preferred. A trap introduced by Thomas, Destappes and Dupont (TDD1) as a development from the copper-foil trap is useful, particularly as it is reported to require (for the dimensions shown) a liquid-air consumption of only 0·3 litre per hour as compared with 2 litre per hour for a conventional design (Fig. 8.4).

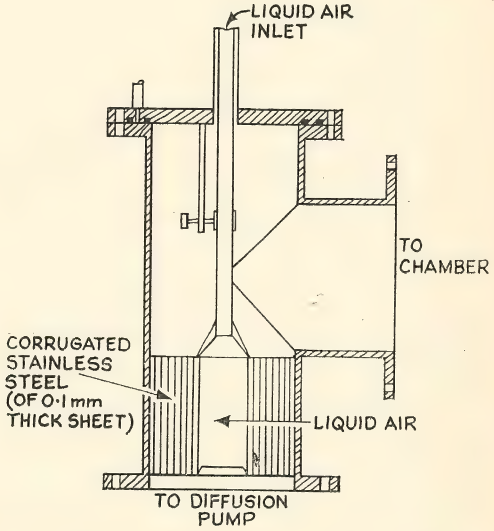


FIG. 8.4 Stainless steel cold-trap with stainless steel corrugated sheet insert (*Thomas, Destappes and Dupont*)

Ultimate pressures of 5×10^{-7} torr can certainly be achieved by such means, but lower pressures demand the degassing by baking of the metal vacuum chamber. This is often difficult especially for chamber volumes above 10 litre. Even a moderate temperature rise to 100° or 200° C is worth while to improve the ultimate vacuum attainable. This can be arranged by the use of an oven, thermal tapes or, in some cases, an internal radiant heater may be installed.

At the October 1958 symposium of the American Vacuum Society, held at San Francisco, details were given of plant for producing residual pressures of 2 to 6×10^{-10} torr in a system volume of 10 to 20 litres. The experimental work in question was on the maintenance of extremely high temperatures in an ion plasma for studies of thermonuclear fusion reactions. The presence of impurities in the plasma may well result in a lowering of its temperature by 10 times or more. To attain such ultra-high vacua, the apparatus had to be baked out repeatedly at 450° C. The demountable vacuum joints used employed gold wire gaskets of 0·02 to 0·03 in. dia which was reduced to 0·01 in. under flange pressure. The finish of the flange surfaces mated on the gold was to a tolerance of 16 micro-inches and a clearance radius of 0·002 in. was allowed for the gold wire. Such joints of up to 8 in. dia withstood 40 to 60 bake-outs each of 12 to 20 hours duration. Glass to Kovar seals (*e.g.* for observation windows) were made by induction-heating, and Kovar-to-metal joints were welded in a helium arc. The high alumina ceramic COORS A1200 was employed for the insulation of electrical connections.

The pumping system comprised a 4 in. metal fractionating oil diffusion pump with two liquid nitrogen traps in series providing an effective pumping speed of 10 to 15 litre per sec (5% of the unrestricted speed) and an ultimate pressure of 2 to 6×10^{-10} torr in a volume made up from glass tubing with a surface area of 10,000 to 20,000 sq cm for a volume of 10 or 20 litres. Using the methods of making unions already specified, the rate of gas influx was 10^{-15} litre-torr per sec per sq cm of surface. It is hoped to build a system volume consisting of 40 ft of 8 in. dia tubing in which an ultimate pressure of 10^{-10} torr is attained by the development of this procedure.

Most of the work in the ultra-high vacuum range below 10^{-8} torr has been with glass apparatus, though small stainless steel vessels have been used as well and glass-to-metal seals are often incorporated. The techniques which have been developed may be listed as follows:

(*a*) The use of a diffusion pump with two cold-traps where the one nearest the chamber is degassed by baking before filling with liquid air or liquid nitrogen.

(*b*) The chamber is first evacuated by conventional pumps to 10^{-7} torr or less, isolated from the diffusion pump by a greaseless metal or glass valve, or sealed off by glass-blowing, and the pressure is then reduced by electrical pumping with an ionization gauge of either the hot-cathode or cold-cathode type.

(*c*) The initial procedure is similar to that for (*b*), the chamber is isolated from the conventional pumps and then either (*i*), a getter (preferably barium or titanium) is fired in the chamber or (*ii*), a bulk getter in the form of a zirconium or, in some cases, molybdenum wire is used, or (*iii*), a getter-ion pump is operated.

(*d*) The initial pressure need be only about 10^{-3} torr as produced by a mechanical rotary pump and the subsequent pressure reduction to very low values is by means of surfaces refrigerated with liquid helium.

To measure pressures down to 10^{-10} or even 10^{-11} torr, the Bayard–Alpert type of hot-cathode ionization gauge in which the X-ray effect is minimized (§ 3.9) is widely employed. It must be stressed that all ionization gauges have an electrical pumping action (§ 6.16) which, indeed, is used to attain ultra-high vacua in accordance with technique (*b*). In measuring the pressure, this must be taken into account or reduced to a minimum. If the ubiquitous Bayard–Alpert gauge is used, for example, then either the electrode accelerating potential should be applied momentarily or, and especially if continuous recording is necessary, the gauge electron current must be reduced to a few microamperes to ensure that the electrical pumping action is negligible. This, of course, does not apply if the gauge itself is used as a pump, but certainly does apply if it is used to monitor the pumping action of another gauge or device. The gauge must also be thoroughly degassed: in the Bayard–Alpert design this is accomplished by electron bombardment of the grid to heat it to about 1200° C, preferably for about an hour, and it must also, of course, be baked out.

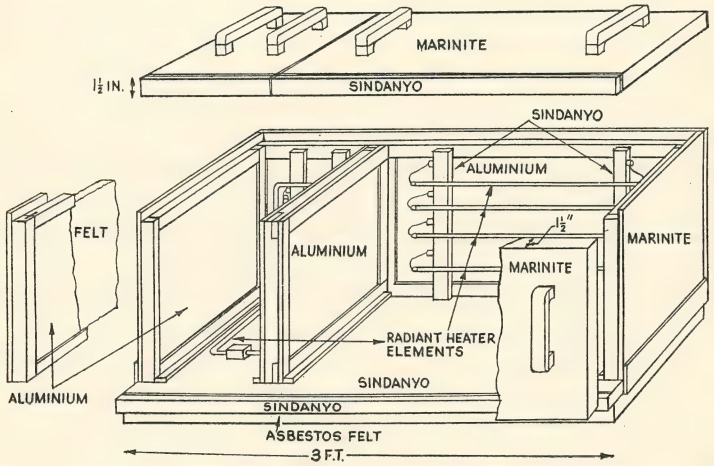


FIG. 8.5 Unit construction bake-out oven with readily removable front and top

(Temperature of 400° to 450° C obtained with power supply of 1 kW per 1½ cu ft)

In the methods (*b*) and (*c*) a greaseless isolation valve which can be baked out is necessary. This is best an ultra-high vacuum valve of the Alpert type or a development therefrom (§ 5.9). In many cases the much more readily made and cheaper greaseless glass hemispherical valve (§ 5.10) can be used, but it will have a larger (though usually insignificant) conductance when closed and, moreover, unlike the Alpert type, cannot be employed as a gas-metering device.

In all cases where an ultimate pressure less than 10^{-8} torr is the aim, a long term bake-out of the system is essential. This should be at 450° C for borosilicate glasses like Pyrex and Hysil and for at least 4 hours and preferably overnight. It is worth mentioning that bake-outs are cumulative in their degassing effect provided that gas is not admitted to the system at a pressure of above about 10^{-4} torr between bakes. Thus, two bakes at separate times of, say, 4 hours each are as effective as a single 8 hour bake provided that the system is continuously under vacuum.

Conventional ovens may be used, but the unit construction developed by Alpert (A12) is convenient. An example which has been used by the authors is shown in Fig. 8.5.

8.2. System Comprising a Diffusion Pump with Two Cold-Traps

A system of this kind in which the trap nearest the chamber is baked out before filling with liquid-air can be used to attain ultimate pressures of 10^{-8} torr with certainty, and 5×10^{-9} torr, as measured by a Bayard–Alpert gauge, or even somewhat lower is possible, especially if all glassware is scrupulously cleaned and maintained clean during assembly (glass-blower's spittle should be avoided by encouraging the use of a drying tube!) and the mercury in the diffusion pump is freshly distilled before filling or, alternatively, a self-fractionating oil diffusion pump is employed. A suitable set-up is illustrated by Fig. 8.6. Note that greased taps are excluded from the inlet side to the diffusion pump. The two traps can be of a conventional design such as that shown in Fig. 2.18(*a*), but the use of a double bulb trap for each (Fig. 8.1) is preferred, though this does demand the services of a highly skilled glass-blower.

A similar set-up is described by Dushman (D1) and is attributed to Apker, who recommends that both traps be baked before the liquid air is applied. He claimed an ultimate pressure of 10^{-8} torr as recorded by a conventional ionization gauge, but this was possibly an overestimate of the pressure as this work was done previous to the introduction of the Bayard–Alpert gauge able to record pressures down to 10^{-10} torr (*see* § 3.9). The introduction of gas to the system of Fig. 8.6 is best via an Alpert-type ultra-high vacuum valve, the use of two such valves separated by a tube being preferred (§ 5.17), where the whole gas inlet train (except, of course, the gas reservoir) can be baked.

The procedure is as follows: first, the glass chamber, the Bayard–Alpert gauge and the cold-trap are given a long-term bake-out at 450° C. Towards the end of this bake, liquid air is put in the lower trap (this may also be baked initially but a separate oven is then necessary, or it may be heated by wrapped-round thermal tapes). After removing the oven, a Dewar flask containing liquid-air is raised to be around the upper trap and then the gauge electrodes are degassed by electron bombardment and any other metal parts within the vacuum chamber are degassed by induction-heating. The chamber alone may then be baked again to release any gas which might have become sorbed in its wall during electrode degassing. If it is required to seal off this chamber from the pumps, then the pre-arranged constriction in its pumping tube must be first degassed by heating for several minutes to nearly the softening point of the glass, and pumping continued subsequently for an hour or two before the final seal-off.

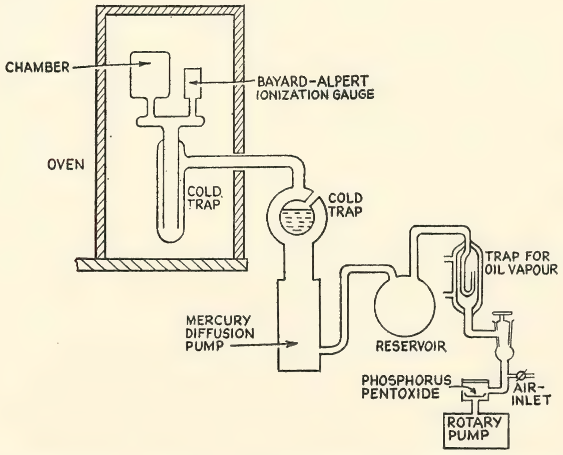


FIG. 8.6 Ultra-high vacuum system utilizing a mercury diffusion pump with two cold-traps, one bakeable

The advantage gained from the use of the two traps, apart from the very effective exclusion of mercury vapour from the tube to be exhausted, is that bake-out of the top trap (or of both traps) ensures that sorbed gas and especially water vapour in its glass walls is released before liquid-air is applied. Though the vapour pressure of ice is negligible at the temperature of $-183°$ C of the liquid-air itself, parts of the glass trap and of the tubulation to it have inner surfaces exposed to the vacuum which do not attain this low temperature, and it must be realized that even at $-120°$ C the vapour pressure of ice is 10^{-7} torr approx. This indicates, incidentally, a further advantage of the trap design shown in Fig. 8.1. Apart from the tubulation between it and the vessel, the only part of its surface not cooled to very low temperatures is the inside surface of the outermost wall and any water vapour released from this surface must perforce be refrigerated again if it passes the two bulbs of the liquid-air filled trap and is therefore unable to reach the vessel being exhausted.

In addition to its virtues as a vacuum system, this set-up is strongly recommended as the basic system for use in conjunction with an isolation valve and electrical pumping to achieve very low pressures of 10^{-10} torr or less, which is the subject of the next section, § 8.3.

Before considering these additions, the outstanding experiments of Venema (V2) must be mentioned, though they are too specialized to consider here in detail. By using a mercury diffusion pump and bakeable traps in an elaborate set-up involving a very exacting and prolonged procedure, he attained ultimate pressures of 10^{-11} torr.

8.3. Production of Pressures of 10^{-10} torr and Below by Electrical Pumping

To produce pressures in the region from 10^{-8} to 10^{-10} torr the technique which has received much attention recently is that of using a hot-cathode ionization gauge as a pump, which is primarily due to the work of Alpert and his colleagues at the Westinghouse Research Laboratories in Pittsburgh, U.S.A. (Alpert, A12; Alpert and Buritz, AB1). In this technique, the Bayard–Alpert ionization gauge (§ 3.9) has been much used for electrical pumping and for measurement of the low pressures attained.

The ultra-high vacuum system used (Fig. 8.7) comprises:

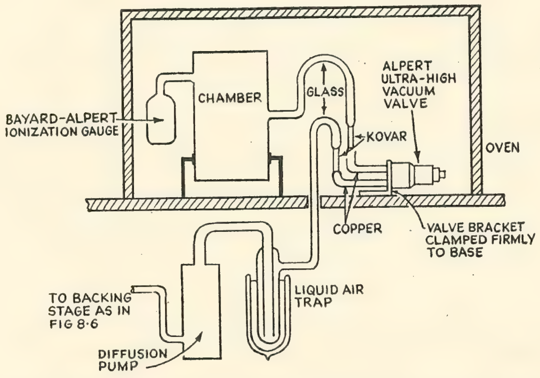

CHAMBER
GLASS
ALPERT ULTRA-HIGH VACUUM VALVE
BAYARD-ALPERT IONIZATION GAUGE
KOVAR
OVEN
COPPER
VALVE BRACKET CLAMPED FIRMLY TO BASE
LIQUID AIR TRAP
TO BACKING STAGE AS IN FIG 8·6
DIFFUSION PUMP

FIG. 8.7 Ultra-high vacuum system for obtaining pressures of 10^{-10} torr

(*a*) The chamber to be evacuated. This must be capable of bake-out at temperatures exceeding 400° C; therefore, it is usually a glass bulb or tube of borosilicate glass, though a stainless steel vessel with metal-gasketed or argon-arc welded seals could be used.

(*b*) A conventional rotary/diffusion pump combination with, desirably, an oil-trap (Fig. 8.3) between the two pumps and also a phosphorus pentoxide trap. Greased taps or Neoprene-seated valves may be employed between the backing pump and the diffusion pump, but certainly not in any circumstances on the high-vacuum inlet side to the diffusion pump. The diffusion pump used by Alpert was a self-fractionating oil diffusion pump in glass; the present authors have used mostly a mercury diffusion pump with a liquid-air trap of the type shown in Fig. 2.18(*a*), but that illustrated by Fig. 8.1 is preferable and, best of all, is the type of system described in § 8.2 with two cold-traps, one of which (that nearest the chamber) is bakeable.

(*c*) A Bayard–Alpert gauge to be used for electrical pumping. This gauge is also usually employed to indicate the pressure, but if a second gauge is used to monitor the pressure it is best to operate it with small electron current (say, 5 μA), so that its pumping action does not confuse the investigation of pump-down rates. This second gauge is, however, unnecessary if the object of the exercise is to produce 10^{-10} torr rather than undertake experimental investigation into electrical pumping. It is not shown in Fig. 8.7.

(*d*) The gauge and the chamber, together with auxiliary directly attached equipment, *e.g.* a gas admittance arrangement, must have an isolation valve between it and the diffusion pump or the cold-trap, if used. This valve has to be baked at 400° C or more and must therefore be a metal ultra-high vacuum valve (§ 5.9) or a greaseless glass valve (§ 5.10).

(*e*) An oven (or ovens), preferably of the unit construction (Fig. 8.5), must be arranged to bake-out at a temperature of at least 400° C the gauge, the chamber together with attachments to it and the valve.

The procedure is as follows:

(*i*) The system is first evacuated to a pressure of about 10^{-6} torr by the rotary/diffusion pump combination. The ultra-high vacuum valve is open. If pressures below 10^{-5} torr cannot be attained either the system is insufficiently clean or leaks are present; in the latter case, leak detection is carried out (*see* Chapter 9).

(*ii*) The gauge, chamber and ultra-high vacuum valve are baked to 400° to 450° C for at least 4 hours and, preferably, for about 12 hours. The longer bake is particularly necessary on first assembling the apparatus or if the system has been previously let down to atmospheric pressure.

(*iii*) Towards the end of the bake-out, the cold-trap (if used) is filled with liquid-air.

(*iv*) After the bake-out, the grid of the gauge is electron-bombarded to raise its temperature to about 1200° C (orange-yellow colour). On first operating the newly assembled system, the temperature should be maintained for about 1 hour, but shorter times of about 20 min can be used subsequently provided the pressure in the system has not increased above about 10^{-3} torr meanwhile.

If the chamber contains internal metal parts (electrodes, filaments, etc.) these must be degassed by induction-heating, direct passage of current or, if possible, by electron bombardment.

After these degassing procedures, the pressure should be reduced to at most 5×10^{-7} torr and preferably 10^{-7} torr or less.

(*v*) The ultra-high vacuum valve is closed and then the gauge run at its normal operating potentials to give an electron current of 1 mA or 10 mA, usually. The pressure will then fall, almost exponentially at first, to reach a value of 10^{-10} torr or less. If the only vessel to be pumped is the ionization gauge itself, which has a volume of about 1 litre, then this pressure drop will take place in about 20 min. A typical pump down curve recorded by F. Baker (*private communication*) is shown in Fig. 8.8. With a chamber attached, considerably longer pump-down times are necessary, but this often does not matter. The pumping speed of the Bayard–Alpert gauge for the gases commonly encountered in vacuum systems is about 0·01 litre per sec for an electron current of 1 mA and increases in proportion to the electron current. For helium, however, it is only about 5% of this value.

According to Alpert (A9), it is possible to attain pressures of about 10^{-10} torr with such systems within 24 hours of its initial assembly. This statement has been verified by the present writers.

Some of the gas removed from the system by the electrical pumping action of the ionization gauge goes to the ion collector but most of it is transported to the inside surfaces of the glass wall of the gauge. The hot tungsten filament of the gauge will also be responsible for clean-up of some reactive gases, particularly oxygen. An amount of gas equivalent to that capable of forming a monolayer can be formed on these surfaces without saturation effects on the pumping action occurring. With the degassing procedure recommended and initial pressures before electrical pumping of 5×10^{-7} torr or less, this saturation is not of practical account in pumping small chambers. However, not all the ions incident on the collecting surfaces will be retained and neutralized; as ions arrive molecules will leave, though this desorption is necessarily less than the sorption otherwise no pumping action would prevail. This desorption is important in practice, however, as the gas tends to be re-evolved if the gauge positive grid potential is reduced to zero. It is therefore necessary to keep the ioniation gauge running continuously to maintain the ultra-high vacuum.

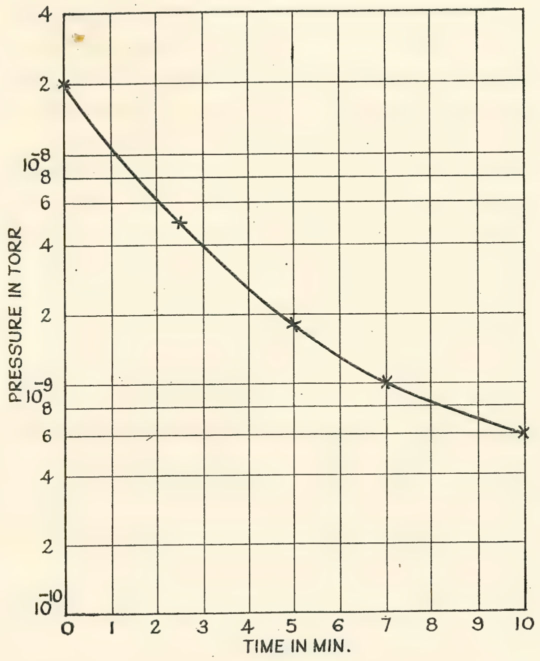


FIG. 8.8 Pressures against time curve obtained on electrical pumping with a Bayard–Alpert type ionization gauge

The rate at which gas is released on switching off the electron current, depends on how effectively the system is degassed in the first place and on the conductance, when closed, of the ultra-high vacuum isolation valve used. In the authors' experience, if a Bayard–Alpert gauge is operated to achieve a pressure of 10^{-10} torr, the subsequent reduction of the electron accelerating grid potential to zero causes gas to be re-evolved at a significant rate, even if the gauge is sealed off from the system by glass-blowing. This seems to be contrary to the experimental data given by Alpert (A9) who records that the rate of the residual pressure rise in a Bayard–Alpert gauge of volume 400 cc can be made a minimum of 3×10^{-11} torr per min (*i.e.* 10^{-3} torr per century) if rigorous initial degassing is undertaken. This very low value has not been achieved in our experiments, probably because the vacuum systems used were not so 'clean'. In practice, therefore, though extremely low rates of pressure rise on switching off the grid potential can be ensured, it is best to keep the gauge running to maintain the ultra-high vacuum in view of the fact that the extremely degassed initial conditions required in the work of Alpert cannot be obtained except by prolonged bake-out.

Alpert and Buritz (AB1) demonstrated that the lowest possible pressure achievable in a glass vessel is limited by the permeation of helium from the atmosphere through the glass wall. The value of this limit will consequently depend upon the pumping speed prevailing and the rate of helium permeation where the latter will be decided by the type of glass and the former by the type of ion-sorption pump and its operating conditions. Using a Bayard–Alpert gauge with a borosilicate glass envelope, the limiting pressure recorded by Alpert and Buritz was 4×10^{-11} torr approx.

Cold-cathode ionization gauges (§ 3.10) can also be used as ion-sorption pumps to produce ultra-high vacua as also can conventional hot-cathode ionization gauges and pumps of the Comsa and Musa type (§ 7.3). In these cases it is usually necessary, however, to use an auxiliary Bayard–Alpert ionization gauge to record the lowest pressures achieved.

Houston (H17) has designed a gauge also useful as an ion-sorption pump in which by the use of combined electric and magnetic fields, the ionizing electrons are made to have average paths of about 10^8 cm at pressures below 10^{-8} torr, leading to considerably enhanced ionizing efficiency. This gauge can produce and record pressures in the range from 10^{-8} to 2×10^{-12} torr. Redhead (R17) has described recently a cold-cathode ionization gauge of the magnetron type in which at the lowest pressures the ionizing electron paths are even much longer and able to record pressures in the range from 10^{-4} to 5×10^{-14} torr.

8.4. Production of Ultra-high Vacua by Getters and Getter-ion Pumps

Total gas pressures as low as 10^{-9} torr can be produced by the use of getters in a thoroughly degassed small glass or ceramic envelope (*e.g.* an electron tube) which is isolated from the conventional pumps either by sealing-off or by an ultra-high vacuum valve. Indeed pressures of these small magnitudes have been shown to exist in satisfactorily processed electron tubes. In electron tube manufacture, the firing of a barium alloy getter (§ 6.10) is the usual procedure. This technique can also be applied with preliminary pumping as described in § 8.3 but where, after the ultra-high vacuum valve is closed, a barium getter is fired instead of (or in addition to) utilizing electrical pumping. It is important to degas the getter and its support by heating to 700° C before the ultra-high vacuum valve is closed; indeed, it is best to deposit some of the getter during the latter stages of this degassing just prior to closing this valve. As an alternative to the use of a flash getter, a bulk getter may be used. In this case, initially thoroughly degassed (at 1200° C) zirconium wire (§ 6.13) is useful, especially if two such wires are employed, one at 400° C (to absorb hydrogen and water vapour) and the other at 1400° C to absorb other gases. The most recently developed technique is to use a getter-ion pump (§ 7.6) with the added advantage that the noble gases, which are not gettered, are transported as ions to the sorbent deposited getter film.

The advantages of the use of flash getters over electrical pumping with an ionization gauge are (*a*) the much greater pumping speed available; (*b*) the greater capacity for gas without saturation of the pump. Thus, a freshly-deposited barium film has a pumping speed of the order of a few litre per sec for a deposit of $10\ \mathrm{cm}^2$ surface area (§ 6.11) as compared with about 0·1 litre per sec for a Bayard–Alpert gauge (§ 7.3). As regards saturation, this is more difficult to assess under practical conditions. As a rough guide, it can be expected that a getter-film of barium or titanium will be able to absorb some 5 monolayers of gas before saturation, whereas the ion collector or glass wall of an ionization gauge used as a pump will exhibit saturation when not more than a single monolayer is formed. This saturation of getter films will depend considerably on the gas concerned, the getter temperature and the evaporation (§ 6.11). Saturation of the pumping action is not important in obtaining pressures down to 10^{-9} torr provided that an initial pressure of less than 10^{-6} torr is attained in a small chamber, irrespective of whether gettering or electrical pumping is used subsequently, because there will then be insufficient gas to form a single monolayer anyhow (§ 6.2). The increased capacity of getters is, however, valuable if gas (of a kind which is effectively gettered, § 6.11) is continuously leaked into the system at low pressure.

The indications are that, despite the above-mentioned advantages of getters, yet lower ultimate pressures can be achieved in small glass systems by electrical pumping because the noble gases (and, in particular, argon, which forms about 1 % of atmospheric air) are not gettered, whereas they are transported (although slowly) in ion-sorption pumps. Thus, experiment shows that a pressure of 10^{-9} torr is readily obtainable by evaporating barium in a small glass chamber which is suitably pre-evacuated and degassed, but that it is difficult to achieve the 10^{-10} torr or less, obtainable by electrical pumping.

Another advantage of the getter is that the sorbed gas is not appreciably desorbed; for an unsaturated barium film, the desorption rate is probably less than 1 % of the sorption rate. In the use of a hot-cathode ionization gauge as a pump, on the other hand, significant desorption of the gas takes place which will cause the pressure in an enclosure to rise on switching off the electrode potentials (§ 8.3).

The use of titanium (and zirconium) getter-ion pumps to achieve pressures of 10^{-8} torr or less is at present restricted to the small glass envelope types (§ 7.6); the large pumps (§ 7.5) cannot be said to have yet realized ultimate pressures below 10^{-7} torr. For the reasons discussed in § 7.6, it is necessary first to reduce the pressure by conventional pumps to 10^{-6} torr or less, degas thoroughly, isolate these pumps from the vessel and the getter-ion pump and then evaporate the titanium with the ionization source switched on. Reich and Nöller (RN1) used a Leybold getter-ion pump (§ 7.6) in the system shown in Fig. 8.9 to attain pressures of 10^{-9} torr and below. After exhaustion with the conventional pumps and degassing, a small amount of titanium was evaporated and when the pressure was 10^{-7} torr approx, the greaseless glass isolation valve was closed. A further 15 min of operation of the getter-ion pump then reduced the pressure to 10^{-9} or, sometimes, 5×10^{-10} torr, the residual gas (as was shown by an omegatron, § 3.13) being primarily argon. A leak-in rate of air of 5×10^{-9} litre-torr per sec to this system could be tolerated over a period of as much as 60 hours, demonstrating the capacity of a titanium film for nitrogen and oxygen.

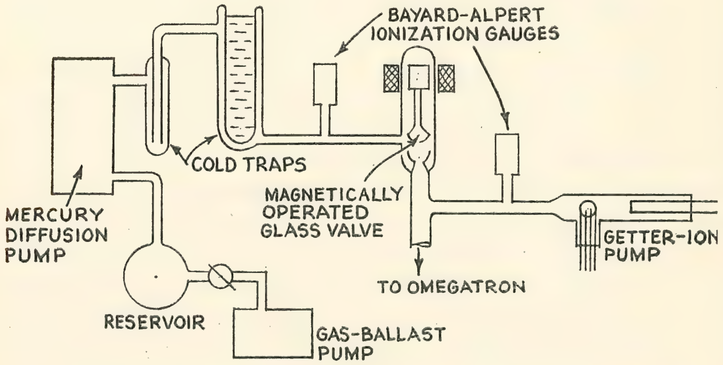


FIG. 8.9 Ultra-high vacuum system using small getter-ion pump (*after Reich and Nöller*)

8.5. The Use of Liquid Helium and Liquid Hydrogen in Ultra-high Vacuum Technology

For many years it has been realized that extraordinarily low gas pressures could be achieved by the use of liquid helium because, at its boiling point of 4° K (−269° C), the vapour pressure of every other gas is insignificant. Simon (S23) points out that the same applies to liquid hydrogen for all gases except helium, neon and hydrogen itself, and he also considers that, by the use of adiabatic demagnetization to produce temperatures of 0·1° K, even the vapour pressure of helium is reduced to 10^{-31} torr.

The possibility of using a surface cooled to liquid helium temperatures as a vacuum pump obviously raises many technical difficulties and severe problems of cost. Nevertheless, development work is in progress in this direction, especially in the U.S.A. and Canada. Redhead (R17) has used a liquid helium cold-trap to attain pressures of 5×10^{-14} torr in studies with small scale plant of his cold-cathode magnetron gauge.

8.6. The Applications of Ultra-high Vacuum

At present, the commercial applications are limited to the use of ionization gauges and small getter-ion pumps for the production of very low pressures in specialized electron tubes during ageing after processing (§ 7.6). Increasing future application may be said to be awaiting developments in the ultra-high vacuum technology of large-scale equipment.

There are, however, a number of research problems (some of which border on industrial application) in which the use of ultra-high vacuum techniques has enabled progress to be made and, where, moreover, a revision of previous results obtained using higher ultimate pressures has been necessary. In general, the ability to produce reliably a total residual gas pressure in the region of 10^{-9} torr affords two main advantages: (*i*) freshly cleaned and degassed surfaces exposed within the vacuum do not become covered with a monolayer of gas in times less than about 2000 sec and, indeed, in small vessels, only enough molecules will be available to form a fraction of a monolayer (§ 6.2); consequently, greatly increased times for experimentation are provided; (*ii*) the small residual gas pressures permit gases admitted to the vacuum to be studied in a very high state of purity.

In connection with (*i*) investigations into the physics and chemistry of surfaces which have benefited are:

(*a*) studies of adsorption, sorption, accommodation coefficients and sticking factors of atoms and molecules;

(*b*) the measurement of work function in relation to the release of electrons by thermionic, photoelectric, secondary and field emission;

(*c*) the effects of incident ions and metastable atoms on surfaces;

(*d*) the effects of gas layers and electrically polarized gas layers, and the removal of such layers, on conductors and semiconductors in relation to contact potential difference, surface conductance and the accumulation and migration of electric charges;

(*e*) the deposition in vacuum of films on solids in relation to the adhesion to the substrate and the measurement of the optical, electrical and magnetic properties of such films; *e.g.* the magnetic properties of nickel–iron alloy films are susceptible to minute quantities of impurities.

As regards (*ii*) mention may be made of the study of ionized gases; as is well known, the mobilities of ions in gases, the electron- and ion-attachment coefficients and the breakdown potentials of gases are all susceptible to very small quantities of impurities, especially those in the form of metastable atoms. In this connection, the development of large ultra-high vacuum systems for the study of thermonuclear fusion reactions in gaseous discharges is likely to receive increasingly energetic attention, as the efficiency with which temperatures in the ion plasma in the range from 5×10^6 to 10^8 °C can be attained is very dependent on the gas purity.

As a final example, accurate recent studies of the permeation of gases through glass (*see e.g.* Norton, N6) have only been made possible by the use of ultra-high vacuum technology.

The subject of leak detection in ultra-high vacuum systems is considered in § 9.11.

9

LEAK DETECTION

9.1. Basic Principles

Consider a chamber of volume V at which the effective pumping speed (*i.e.* the speed of the pump corrected for the conductance of tubulation, isolation valves, etc., § 1.6) is S_e at a pressure p and where the rate at which gas is produced within this chamber at this pressure is Q. Then the rate of reduction of pressure in the chamber $\left(\frac{dp}{dt}\right)$ is given by:

$$\frac{dp}{dt} = -\frac{S_e}{V}p + \frac{Q}{V} \qquad (9.1)$$

Adopting the usual units, V is in litres, p in torr, S in litre per sec, Q in litre-torr per sec and $\frac{dp}{dt}$ is given in torr per sec.

An alternative expression for $\frac{dp}{dt}$ is:

$$\frac{dp}{dt} = -\frac{S_e}{V}(p - p_u) \qquad (9.2)$$

where p_u is the ultimate pressure obtainable in the chamber.

Comparison of equations (9.1) and (9.2) shows, as would be expected, that

$$p_u = Q/S_e \qquad (9.3)$$

In practice, Q will be decided by four factors: Q_L, the gas influx through leaks in the system due to the presence of holes or regions of porosity; Q_V, the influx due to virtual leaks caused by the desorption of gas from the chamber walls, interior parts, and seals; Q_B, the back-streaming of vapour from the vapour pump added to which may be back-diffusion through this pump; and Q_P, the influx due to permeation of gas through the chamber walls.

It is not possible simply to add these various factors together and equate them to Q, since they may well vary with time and, whereas a leak is normally due to the infiltration of air, back-streaming is in the form of the pump fluid, which, moreover, may decompose in the presence of a hot filament or a gaseous discharge; the virtual leak is most usually a condensable vapour and the permeation of the wall material will be different for different gases.

Except for ultra-high vacua (Chapter 8), Q_P can be regarded as zero unless the designer is so unwise as to choose a material like cast brass for a system in which high vacua are to be maintained. Back-streaming is of importance in kinetic systems, especially those using large vapour pumps with neither cold-trap nor efficient baffling and is a source of confusion in leak detection practice, as hydrogen produced on decomposition of the pump oil in contact with a heated filament may not be readily distinguishable from hydrogen used as a search gas (§ 9.5). Virtual leaks are likewise a source of difficulty in kinetic systems, especially those in which the chamber cannot be degassed by bake-out, so the leak-detection apparatus should be able to distinguish between virtual and actual leaks, particularly if pressures below 10^{-4} torr are required. However, the chief topic under discussion in this chapter is actual leakage which contributes to the magnitude of Q_L. If, therefore, the simplification is introduced that Q_V, Q_B and Q_P are negligible compared with Q_L, equation (9.3) becomes

$$p_u = Q_L/S_E \tag{9.4}$$

As an example of the simple application of this equation, consider a common laboratory requirement of obtaining an ultimate pressure of 10^{-5} torr in a chamber at which the effective pumping speed is 10 litre per sec. The maximum tolerable leak-rate is therefore given by:

$$\begin{aligned} Q_L = S_E \,.\, p_u &= 10^{-4} \text{ litre-torr per sec} \\ &= 10^{-1} \text{ litre-micron per sec, } \textit{i.e. } 10^{-1} \text{ lusec.} \end{aligned}$$

As will be seen in the following sections, a leak-rate of this order of magnitude can be found comparatively readily, but note that the problem is made proportionally more difficult as the ultimate pressure required is less, or the pumping speed available is less.

The order of size of leak which must be detectable in a chamber to be sealed off from the pumps and remain under vacuum is, of course, much smaller. For example, consider a vacuum tube of volume 1 litre in which the pressure is initially 10^{-6} torr and where an increase to 10^{-5} torr within 100 hours is the maximum that can be tolerated. In equation (9.1), S_E is now zero, presuming there is no pumping action due to a getter or transport of ions (electrical pumping) in the chamber. Assuming also that the chamber has been thoroughly degassed so that only actual leaks from the atmosphere are concerned, then the maximum tolerable leak-rate is given by:

$$Q_L = V\frac{dp}{dt} = \frac{10^{-5} - 10^{-6}}{100 \times 3600} \text{ litre-torr per sec.}$$

Neglecting 10^{-6} compared with 10^{-5}, then

$$\begin{aligned} Q_L &= 2{\cdot}8 \times 10^{-11} \text{ litre-torr per sec} \\ &= 2{\cdot}8 \times 10^{-8} \text{ lusec.} \end{aligned}$$

This very small leak cannot be detected rapidly except by the most elaborate mass spectrometer techniques (*see* § 9.9).

9.2. Methods of Leak Detection in which a Vacuum Gauge is not Employed

Various simple techniques are available for locating leaks in vacuum systems in which gauges (other than the discharge tube indicator) are not used and where the minimum detectable leak (the minimum gas flow in litre-torr per sec that can be detected) is high in most cases but which are, nevertheless, valuable, especially for testing system components before assembly, and vacuum systems when first constructed. They are:

(*a*) **The isolation test.** The chamber is isolated from the pumps by a tap, valve or cut-off. If a leak is present, then on reconnecting to the pumps after a time interval, the sound made by the rotary pump will change from a hard mechanical note and, moreover, air bubbles will appear in the rotary pump oil. This is a very crude but often useful test which, however, only shows that a leak is present without locating it. Of course, cut-off tests are more satisfactory if a discharge tube indicator or, preferably, a vacuum gauge is used (§ 9.4).

(*b*) **The soap-bubble test.** A layer of soap solution is applied to the outside surface of the component before assembly in the vacuum system. This component is sealed except for a single inlet to which compressed air or other gas is applied. The site of a hole is indicated by a bubble developed in the soap solution. This method can also be applied to the assembled vacuum system before evacuation, but this is usually inconvenient. Generally, it is used for locating leaks in soldered or welded joints in metal tubes and chambers, but will only detect a hole of considerable size; for example, one in which solder has not flowed evenly around a joint.

Guthrie and Wakerling (GW1) point out the advantages of using a light gas in this method because of its higher permeation rate. Hydrogen is a possibility but is inflammable; helium is a good choice but is expensive, at least in Britain. These authors estimate the minimum detectable leak by this method to be 8×10^{-5} litre-torr per sec for air.

It is also possible to pump out the vacuum system, apply the soap solution externally and observe the permeation of this solution through the walls. Guthrie and Wakerling (GW1) consider the rather intriguing idea, applicable only to very large chambers, of requesting a volunteer, equipped with an oxygen mask, to enter the chamber, which is pumped out to about $\frac{3}{4}$ atmosphere, and look for the formation of soap-bubbles; it is, of course, essential to guard against too great a reduction of pressure due to oversight in this case!

(*c*) **The spark-coil detector** is useful for glass vacuum systems or those constructed partly of glass or other non-conducting material. After evacuation by a rotary pump alone to a pressure between about 10^{-2} torr and 3 torr, the exterior surface of the glass is explored by the metal probe of a high-frequency coil (a Tesla coil is usually employed). If the probe is within about 1 cm of a pinhole, a readily visible spark will occur between the probe and the ionized gas within the system. This method is frequently employed to locate pinholes in newly assembled glass systems. After detection, air is admitted to the system to atmospheric pressure, the region of the hole is heated by a blowpipe flame (an oxy-gas flame for borosilicate glasses) and then a glass rod of which the tip has been pre-heated is approached to draw away molten glass from the immediate vicinity of the hole. It is no use just to heat the glass around the hole and expect it to become sealed. Alternatively, a temporary repair may be effected by applying W-wax to the slightly warmed (50° C) glass in the location of the pin-hole.

If, on exciting the discharge, a pink glow is observed, the presence of nitrogen is indicated and a leak (or inadequate pumping) should be suspected.

The use of a Tesla coil suffers from the disadvantages that it can only be used over the limited pressure range from about 10^{-2} torr to, perhaps, 5 torr, that it cannot be used to locate leaks in metals or metal-glass seals and that too fierce a spark discharge (max length should be $\frac{1}{2}$ in.) from the probe may puncture the glass, especially if it is held too long at one place or thin glass has been left by an unskilled glass-blower.

(*d*) **The discharge tube indicator.** Either an auxiliary discharge tube is connected to the vacuum system and a glow excited within it by a p.d. of at least 2 kV r.m.s. a.c. across its electrodes or a discharge glow is set up by a Tesla coil applied to this discharge tube, or to a suitable part of the glass tubulation of the system. This discharge tube, or the glass tube to which the Tesla coil is applied, is preferably attached to the backing side of the vapour pump (if used), since any air leaking into the vapour pump inlet side (*i.e.* fine side) of the system will be compressed to an increased pressure within the backing space by the action of the vapour pump. Moreover, if the inlet side pressure is less than 5×10^{-3} torr, it will be difficult to excite the discharge there.

After exciting the discharge, which will be pink in colour if nitrogen is present, but bluish-white at pressures less than 10^{-2} torr, the surface of the system (which can now be mostly constructed of metal, if required) is explored by a search gas. This is best a jet of carbon dioxide or methane, but a simpler provision, though less satisfactory, is in the form of a rag, or preferably a piece of cotton wool wound around the top of a glass rod, soaked with alcohol; petrol and benzol, also blue methylated spirits—which contains pyridine—should *not* be used, as they adhere to glass. When a leak is reached, the colour of the discharge will be observed to change. For carbon dioxide, the colour of the positive column in the discharge changes to bluish green; for alcohol, it becomes bluish-white. A method of improving the sensitivity is to study the discharge with a spectroscope and note the change in the spectrum rather than rely on simple visual observation. The method is not considered very satisfactory and attempts to improve its sensitivity (as by the use of a spectroscope) are vitiated by the release of occluded glasses from the walls of a discharge tube which has been in use for some time.

Lloyd (L13) has designed a simple audible leak detector ('squealer') based on a discharge tube. This tube is connected in series with a loudspeaker and a combination of a condenser (0·001 μF) with resistor (1 MΩ) in parallel across a 900 V d.c. supply to provide a simple relaxation oscillator circuit. The discharge tube itself was in the form of a metal cylinder as cathode with a central axial wire as anode (similar to a Geiger–Müller tube). As the gas pressure in this tube varied from 5×10^{-2} to 10 torr, the frequency of the note produced by the oscillator altered over the range from 1 kc/s (at 5×10^{-2} torr) to 2·5 kc/s (at 0·4 torr) and then decreased continuously down to about 100 c/s at 10 torr. A reference oscillator of similar design with a sealed discharge tube proved useful as a reference in that it provided a constant frequency audible note. This method of leak detection was used successfully in the pumping and testing of Geiger–Müller tubes; indeed, such a G.M. tube could also be used as the discharge tube.

(*e*) **The glow discharge method for sealed vessels.** A method which has not been employed much but which might well find greater application because it is simple and inexpensive is concerned with the testing of vacuum-tube envelopes, and especially of metal-to-glass seals in them. This procedure is a long-term one, but it could be useful in quality control. For example, suppose a type of lamp or electron tube utilizes sealing (*e.g.* metal-to-glass or ceramic or metal-to-metal) which has not been exhaustively tested under production conditions. It is important to ensure long life of this tube, *e.g.* at least 1000 hours. As will be seen from the calculation given in § 9.1, a leak rate of only about 3×10^{-12} litre-torr per sec can cause the pressure to rise to 10^{-5} torr in 1000 hours, and this may well be inadmissible. Such a small leak cannot be detected rapidly by even the most sensitive means. A possibility is to give a predetermined fraction of the tubes being made (say 2%) a shelf-life test over a period of, say, 6 months. In some cases, it would then be possible to determine the pressure rise during this time by operating the internal electrodes as an ionization gauge; an alternative is first to evacuate the samples to 10^{-4} torr or less, degas by baking and then fill them with neon at a pressure of about 1 torr. After the long-term standing, these samples are then tested with a Tesla coil (part of the envelope must be transparent) and the colour of the discharge glow obtained compared with that of a similar standard tube which is known *not to leak*. If a sample has leaked during the shelf-life, the neon discharge will show a slight change of colour towards pink, which is easily detected against the standard. Tests carried out by Pirani in conjunction with Leemans (*unpublished*) indicate that an increase in pressure due to leak-in of air from 1 torr to 1·01 torr is shown up in this way. Over a period of 6 months, for an enclosure of volume 50 cc, this corresponds to the detection of a leak of approx 7×10^{-12} litre-torr per sec.

In the use of such tests, the provision of standard tubes which do not leak could be undertaken by dipping half, say, of a sample batch in a molten resin (*e.g.* the glycerine-phthalicacid polymer known as 'glyptal' or 'peralac', alternatively, 'saran' from *Dow Chemicals Ltd.*) which contains no solvent.

(*f*) **Miscellaneous leak indication methods.** A simple method useful for glass apparatus is to paint on the suspected areas a 10^{-5} M to 10^{-6} M alcoholic solution of fluorescein or eosin (Volcker, V3). After 2 or 3 min the surplus solution is removed and the surface exposed to ultra-violet light, *e.g.* from a mercury lamp. Holes and other surface defects into which the fluorescent solution has penetrated will be immediately evident.

Some indicator methods worthy of investigation are:

(*i*) To utilize the fact that molybdenum oxide (MO_3) films change colour from white to dark blue when exposed to atomic hydrogen. An oxidized molybdenum film produced by vacuum deposition on a plate could be used, or MO_3 crystals stuck on a glass plate, and the surface of the vacuum system explored with a jet of hydrogen, and a discharge or heated filament or irradiation with ultra-violet light (*e.g.* at 2537 Å from a quartz mercury lamp) used to dissociate the hydrogen into the atomic state.

(*ii*) Filaments of tantalum or titanium absorb hydrogen markedly when heated (§ 6.13). The consequent change of resistance of the filament would serve to denote that hydrogen had reached the wire via a leak.

9.3. Characteristics of Leaks

Before considering the methods of leak detection and measurement which employ vacuum gauges and gas analysers, it is necessary to examine more specifically the characteristics of leaks, particularly as gauge methods often permit the actual magnitude of the leak to be given.

A considerable variety of units are employed in the literature in specifying leak rates. In this text, the unit litre-torr per sec, implying one litre of the gas concerned (often air) at a pressure of one torr which traverses the leak in one second, will be adopted. Table 9.1 is given to show the ratios of this unit to the others frequently quoted.

For kinetic vacuum systems, especially large ones, an agreed leak-rate is often specified in the design. At 10^{-6} torr this may be, say, 100 cu ft micron per hour, equal to $7{\cdot}9 \times 10^{-4}$ litre-torr per sec. The pumping speed required would therefore have to be at least $7{\cdot}9 \times 10^{-4} \times 10^{6}$, *i.e.* 790 litre per sec to maintain the required vacuum. If, however, a pressure of only 10^{-5} or 10^{-4} torr is required then, correspondingly, minimum pumping speeds of 79 and 7·9 respectively would be adequate. In the Birmingham cyclotron, for example, the leak rate is quoted as 0·01 lusec, equal to 10^{-5} litre-torr per sec. For vacuum plant used in metal casting, for example, with a repetition cycle of, say, 30 min, a leak of 10^{-3} litre-torr per sec is often admissible.

As mentioned in § 9.1, it is important to distinguish between real and virtual leaks. The chief characteristic of a real leak is that, if the pumps are isolated from the region of the system in which a real leak is present, then the pressure in this region will rise continuously with time. In the case of a virtual leak in the same circumstances, the pressure will increase exponentially with time and the pressure–time curve will tend asymptotically to a final pressure. The commonest cause of virtual leaks is water vapour. If free water is present in the system, then the final pressure will be the vapour pressure of water at the temperature concerned, *e.g.* 13 torr at 15° C. If, as is more often the case, the water is absorbed in the surfaces of the vacuum tank walls, then there will not usually be sufficient water present to give such high pressures, but the virtual leakage will, nevertheless, cause an exponential rise of pressure to some upper limiting value depending on the amount of water concerned and the volume of the tank.

In this connection, a clean brass tank after pumping for some 15 min would show a virtual leak of about 10^{-2} litre-torr per sec per sq m of interior

TABLE 9.1

Units of leak-rate

Unit[1]	litre-torr per sec	litre-millibar per sec	litre-micron per sec	litre-S.T.P. per sec	cu ft-torr per sec	cu ft-micron per sec	cu ft-S.T.P. per sec	gram[3] of air per sec
litre-torr per sec	1	1·33	10^3	$1{\cdot}32 \times 10^{-3}$	$3{\cdot}53 \times 10^{-2}$	35·3	$4{\cdot}66 \times 10^{-5}$	$1{\cdot}59 \times 10^{-3}$
litre-millibar per sec	0·75	1	750	$9{\cdot}9 \times 10^{-4}$	$2{\cdot}65 \times 10^{-2}$	26·5	$3{\cdot}5 \times 10^{-5}$	$1{\cdot}2 \times 10^{-3}$
litre-micron[2] per sec	10^{-3}	$1{\cdot}33 \times 10^{-3}$	1	$1{\cdot}32 \times 10^{-6}$	$3{\cdot}53 \times 10^{-5}$	$3{\cdot}53 \times 10^{-2}$	$4{\cdot}66 \times 10^{-8}$	$1{\cdot}59 \times 10^{-6}$
litre S.T.P. per sec	760	1014	$7{\cdot}6 \times 10^5$	1	26·8	$2{\cdot}68 \times 10^4$	$3{\cdot}53 \times 10^{-2}$	1·205
cu ft-torr per sec	28·3	37·6	$2{\cdot}83 \times 10^4$	$3{\cdot}74 \times 10^{-2}$	1	10^3	$1{\cdot}32 \times 10^{-3}$	$4{\cdot}5 \times 10^{-2}$
cu ft-micron per sec	$2{\cdot}83 \times 10^{-2}$	$3{\cdot}76 \times 10^{-2}$	28·3	$3{\cdot}74 \times 10^{-5}$	10^{-3}	1	$1{\cdot}32 \times 10^{-6}$	$4{\cdot}5 \times 10^{-5}$
cu ft-S.T.P. per sec	$2{\cdot}15 \times 10^4$	$2{\cdot}86 \times 10^4$	$2{\cdot}15 \times 10^7$	28·3	760	$7{\cdot}6 \times 10^5$	1	34·2
gram of air per sec	$6{\cdot}3 \times 10^2$	$8{\cdot}3 \times 10^2$	$6{\cdot}3 \times 10^5$	0·83	22	$2{\cdot}2 \times 10^4$	$2{\cdot}9 \times 10^{-2}$	1

[1] For all units, to convert time unit from second to minute, multiply by 60; and from second to hour, multiply by 3600.

[2] Litre micron per sec = 1.μ/sec, known as the *lusec*; as the term 'lusec' is misleading dimensionally, the word *lupersec* might be preferred. 1 *clusec* = 0·01 lusec.

[3] For dry air at 20° C.

plant often shortens considerably the search time. If the rate of increase of pressure $\left(\frac{dp}{dt}\right)$ is recorded for a known total volume of the isolated part of the system (including the gauge volume which, however, may often be neglected in rough estimations) the leak rate can be calculated. Equation (9.1) applies where S_e is zero and Q equals Q_L; therefore,

$$\frac{dp}{dt} = \frac{Q_L}{V}.$$

Very small leaks can be measured in this way by simply employing sufficiently long times of cut-off to enable very small values of $\frac{dp}{dt}$ to be recorded (though confusion with virtual leaks will occur unless the system is clean and degassed). For example, suppose the pressure rise is uniform from 10^{-5} torr to 10^{-3} torr in one hour and the volume V is 5 litre, then:

$$Q_L = 5\left(\frac{10^{-3} - 10^{-5}}{3600}\right) = 1{\cdot}4 \times 10^{-6} \text{ litre-torr per sec.}$$

It would, however, usually be difficult to locate so small a leak by the simple coverage procedure described.

If a virtual leak is concerned instead of a real one, the gauge reading will tend to a limiting maximum value after some time instead of increasing continually. However, this limit will only be recorded satisfactorily if a gauge is used which responds to the total pressure (*i.e.* excluding the McLeod gauge, though the method of § 3.4 could be of some value) and, moreover, confusion often arises in detecting small leaks because both real and virtual leaks may be present.

9.5. The Principles Involved in the Use of a Search Gas in Leak Detection

A valuable and widely used technique of leak detection is to expose the exterior surface of the vacuum system to a search gas (*i.e.* probe gas) or vapour so that, if a leak is present, this gas enters the system and displaces some of the residual gas in the neighbourhood of a pressure-sensitive element in the vacuum.

There are several variations of this general technique depending chiefly on the detector element used, but these various methods have a number of features in common.

The detector element is either a vacuum gauge or a gas analyser (sometimes known as a 'vacuum analyser'). Those vacuum gauges which have been used most are the Pirani gauge (the thermocouple gauge is an alternative) and the ionization gauges of both the hot- and cold-cathode types. The most sensitive methods employ a device which can analyse gas mixtures into ionized molecules of various mass/charge ratios, *i.e.* a mass spectrometer. Of the many types of mass spectrometer, the ones used in leak-detection practice are the Dempster type (in which accelerated positive ions are deflected through 180° in an analysing magnetic field), the Nier type (in which the deflection is through 60° or 120°), the radio-frequency mass spectrometer and the omegatron.

The search gas chosen depends on a number of considerations outlined later. In general, for use with a Pirani gauge or an ionization gauge, the maximum sensitivity is obtained by the use of butane (Calor gas). Hydrogen is, however, often used and carbon dioxide is a popular choice as it is non-inflammable. If the detecting element is a mass spectrometer then helium is the best search gas, but considerable work has been done with the much cheaper hydrogen, argon, and also with methane.

Certain basic theoretical considerations apply to the search gas technique. Consider a simple vacuum system consisting of a chamber of volume V to which is connected a vacuum pump of speed S which is reduced to an effective speed S_e by the conductance U of the tubulation between the chamber and the pump (Fig. 9.1). Suppose a leak of throughput Q_L is present at the chamber in which the pressure is p. Then, in the steady state:

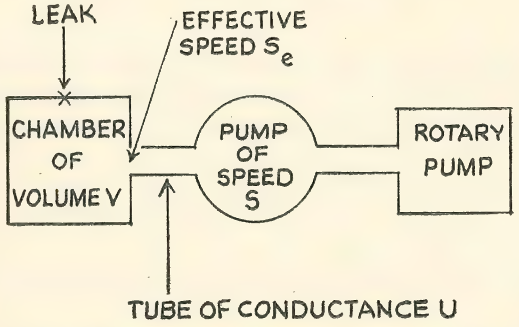


FIG. 9.1 Concerning the theory of leak-detection by a search gas applied to a simple vacuum system

$$Q_L = S_e p \tag{9.9}$$

Considering only viscous flow through the leak (*i.e.* values of Q_L greater than 10^{-5} litre-torr per sec, § 9.3), equation (1.20) applies for the conductance of the leak and hence:

$$Q_L = \frac{BP^2}{\eta} \tag{9.10}$$

where B depends only on the geometrical dimensions of the leak, η is the viscosity of the gas and P is the external pressure (normally one atmosphere) which is much greater than p.

In the process of leak-detection, a search gas is applied to the leak so the exterior gas will be a mixture of air and this gas (Fig. 9.1). Following Blears and Leck (BL2), let the concentration of the search gas be x atmosphere ($x < 1$) so that of the air is $(1 - x)$ for a total external pressure of one atmosphere. If $Q_L = Q_x$ and $\eta = \eta_x$ for this mixture of gases, equation (9.10) becomes:

$$Q_x = \frac{BP^2}{\eta_x} \tag{9.11}$$

In equation (9.9) let $S_e = S_A$ and $p = p_A$ for the air in the gas mixture and $S_e = S_S$ and $p = p_S$ for the search gas. Then Q_x is also given by:

$$Q_x = S_A p_A + S_S p_S \tag{9.12}$$

A characteristic of a viscous leak is that a concentration x of a gas outside the leak will give rise to the same fraction x of molecules of this gas entering the vacuum. It follows that:

$$\frac{BP^2}{\eta_x}(1 - x) = S_A p_A$$

and

$$\frac{BP^2}{\eta_x} \cdot x = S p_S$$

The total pressure inside the volume V is therefore given by:

$$p_A + p_S = \frac{BP^2}{\eta_x}\left(\frac{1 - x}{S_A} + \frac{x}{S_S}\right) \tag{9.13}$$

If the vacuum gauge is connected to the volume V, when x changes from zero (search gas absent) to a concentration x (search gas present) the change in pressure of the search gas at the gauge is Δp_x, given by:

$$\Delta p_x = BP^2\left[\frac{1}{\eta_x}\left(\frac{1 - x}{S_A} + \frac{x}{S_S}\right) - \frac{1}{\eta_A S_A}\right] \tag{9.14}$$

where η_A is the viscosity of air.

This becomes a maximum of Δp_m for $x = 1$ (only search gas present at the leak) given by:

$$p_m = BP^2\left(\frac{1}{\eta_S S_S} - \frac{1}{\eta_A S_A}\right) \tag{9.15}$$

where η_S is the viscosity of the probe gas.

Suppose now that the vacuum gauge has a sensitivity of K_A for air and K_S for the search gas. The maximum change in the gauge reading, ΔG, on applying the search gas is therefore seen to be, from equation (9.15):

$$G = BP^2\left(\frac{K_S}{\eta_S S_S} - \frac{K_A}{\eta_A S_A}\right) \tag{9.16}$$

The British Standards Institution (B.S.I. 2951: 1958) defines the *sensitivity of a leak-detecting element* as 'the deflection of the indicator when, at the position of the element, unit partial pressure of air is exchanged for unit partial pressure of search gas'. For the sensitivity to be a maximum it follows, on studying equation (9.16), that the practical requirements are:

(*i*) complete coverage of the leak by the search gas;
(*ii*) high sensitivity of the gauge for the search gas, *i.e.* large K_S;
(*iii*) a low value of η_S, the viscosity of the search gas;
(*iv*) a small value of the effective pumping speed, S_S, for the search gas;
(*v*) as S_S depends on U, the conductance of the tubulation, and U is proportional to $M^{-\frac{1}{2}}$, where M is the molecular weight of the gas (equation 1.17), the search gas should have a high molecular weight to restrict the value of U.

Consider first requirement (*iv*), *i.e.* a small value of S_S. This can be achieved by the use of a slow pump, *e.g.* a small rotary pump. However, such pumps suffer from considerable speed fluctuations and, moreover, will provide ultimate pressures of only about 10^{-3} torr. It is therefore desirable to use a faster pump and restrict its speed—and also pressure fluctuations—by increasing the tubulation conductance U. The preferred practice, however, is to use a diffusion pump with a rotary backing pump, as diffusion pumps give pressure fluctuations of only about 2% of the mean value with a period of 1 to 10 second, and then reduce the pumping speed by means of U.

However, U cannot conveniently be made too large as otherwise the response time of the leak-detector will become excessively long because it will require time for the gas within the system to become predominantly the search gas (for a study of the differential equations involved in considering pressure changes, *see* Guthrie and Wakerling, GW1, and Turnbull, T3) and the B.S.I. recommendation is that 'not more than 3 seconds must elapse between covering the leak and reading the deflection', in comparing the sensitivities of leak detection methods.

Again, in considering the value of U, a distinction is necessary between two cases in practice: (*a*) the search gas is applied to a vacuum system to which a suitable gauge is attached and the plant concerned is designed either for general laboratory use or for some particular task like vacuum coating, metallurgy, etc.; (*b*) a special vacuum plant is constructed for leak-detection purposes and apparatus (*e.g.* tanks, vacuum tubes, valves, tubing, seals, etc.) is attached to this leak-detector unit so that it can be tested before use.

In both these cases, the same considerations hold with regard to the search gas and the gauge in relation to requirements (*i*), (*ii*), (*iii*) and (*iv*). However, greater freedom of design is possible in the case of vacuum plant designed specifically for leak-detection purposes in regard to an optimum choice of U, the tubulation conductance. In the case where leak detection is performed on vacuum plant designed for other purposes, the object of the design is frequently to make the effective pumping speed as large as possible, necessarily leading to decreased leak-detection sensitivity. This situation can be improved, however, if the isolation valve or tap between the pump and the chamber can be only partially opened, so introducing a high impedance to gas flow during leak detection.

The best choice of search gas in relation to requirements (*i*) to (*v*) can only be arrived at by experiment. Hydrogen is often used with a Pirani gauge as it satisfies more than other gases the requirements (*ii*) and (*iii*) because it has low viscosity and high thermal conductivity. These advantages are, nevertheless, offset by its low molecular weight so that (*v*) is not fulfilled. Coal gas can be used instead of hydrogen, but it will give lower sensitivity. These two gases are not a good choice, moreover, in the attempt to provide good coverage of the leak (*i*). To arrive at the best search gas by experiment, Blears and Leck (BL2) introduce a *substitution sensitivity factor* (ϕ) defined by:

$$\phi = \frac{\text{change of pressure caused by covering the leak with the search gas}}{\text{mean air pressure before probing}}$$

The experimental values of ϕ determined for a Pirani gauge and for a hot-cathode ionization gauge are given in Table 9.2.

TABLE 9.2
Substitution sensitivity factors, ϕ

Search gas	Hot-cathode ionization gauge	Pirani gauge
Butane	10	1
Diethyl ether	5	0·7
Carbon dioxide	1	0·3
Carbon tetrachloride	1	0·05
Benzine	0·3	0·1
Hydrogen	−0·4	0·4
Coal gas	0·25	0·25

The gases are preferred to the liquids diethyl ether, carbon tetrachloride and benzine, as these liquids may block the leak or may enter the vacuum system in considerable concentration through a large leak and have considerable affinity for glass. Hence the most suitable gas is butane, C_4H_{10} (Calor gas) which has low viscosity, high molecular weight, good thermal conductivity and high ionization probability. For an ionization gauge, the second best choice is carbon dioxide, whilst for a Pirani gauge it is hydrogen. Carbon dioxide has the practical advantage, compared with butane and hydrogen, of being non-inflammable.

The minimum detectable leak, $Q_{L\min}$, *i.e.* the smallest throughput of air (or mass flow per unit time) that can be unambiguously recorded by a given leak detector, will depend on the method used and on pressure fluctuations within the vacuum system. Blears and Leck (BL2) point out the simple relationship

$$Q_{L\min} = \frac{\Delta p_A \,.\, S_A}{\phi} \tag{9.17}$$

where Δp_A is the pressure fluctuation and S_A is the effective pumping speed for air at the detector. If, therefore, in a certain leak detection plant the speed S_A is 5 litre per sec, the air pressure fluctuation is known to be 2×10^{-6} torr at a mean pressure of 10^{-4} torr and an ionization gauge is used with butane as the search gas, ϕ is seen to be 10 (Table 9.2) and from equation (9.17).

$$Q_{L\min} = \frac{2 \times 10^{-6} \times 5}{10} = 10^{-6} \text{ litre-torr per sec.}$$

9.6. The Application of the Search Gas

Irrespective of which leak detection method is used, similar considerations apply to the method of using the search gas. The data following is based on suggestions by Ochert and Steckelmacher (OS2) and also Guthrie and Wakerling (GW1). They apply to the use of leak detection plant with a search gas (rather than a vapour) like butane, hydrogen or carbon dioxide or, for mass spectrometer leak detectors, helium. In using butane and hydrogen care must be taken to avoid the accumulation of ignitable or explosive mixtures in the vicinity of a flame; if helium is used, conservation of supplies is necessary because of economy.

For single vessels and components, the top flange of the diffusion pump is sealed to a horizontal large flat metal plate with a central aperture of the same size as the pump baffle valve opening. It is then useful to have available a set of flat metal discs of diameter about 1 in. greater than that of the baffle valve. Each of these discs has a central hole, the set of plates providing a range of hole sizes. The appropriate disc (*i.e.* with a central hole size chosen in relation to the vessel or component under test) is then sealed on to the top plate by pressing Apiezon 'Q' compound or silicone putty around the edge of the disc. A vessel, pipe closed at one end, or other article may then be sealed over the aperture of the appropriate size either by a rubber gasket or again by vacuum putty. A further range of adaptors based, for example, on O-ring seals or on conical joints must also be available, depending on the geometry of the component under test.

Leaks may be hunted with a jet of search gas (rate of travel of probe: about 1 in. in 20 sec) or, alternatively, a hood test may be used. If the **hood test** is convenient, it is undertaken first to denote whether or not a leak is present; if there is a leak, then the probe test is performed to locate the leak. In the hood test, the article concerned is connected to the leak-detection plant by the appropriate vacuum union and then either a bell-jar with an L-gasket seat is placed on the flat plate over the article and search gas (preferably hydrogen or helium) admitted via a side-tube in the bell-jar, or the article is enclosed within a bag of gas-tight material to which the search gas is admitted. Balloon fabric is a suitable material; plastics can also be used, but it should be ensured that they give no danger of sparks due to frictional charges if an inflammable search gas is used.

To leak-test a number of small similar articles, *e.g.* electron tube envelopes, a manifold connected to the inlet of the diffusion pump is recommended (Fig. 9.2). In mass production it is usual simply to find out if the article is leaking and reject it; the exact location of the leak is not necessarily important. The practice is therefore to arrange individual hoods for the articles, of which as many as a dozen may be conveniently tested together on one plant. Cup-shaped components or those with comparatively large openings are arranged on plate or other suitable unions on the manifold, and placed over each component is a hood which is first roughly evacuated by an auxiliary rotary pump and then filled with search gas. For completely enclosed components, like small electron tube assemblies with a narrow pumping stem of high impedance to gas flow, simple fitting rubber hose (lubricated inside with Apiezon oil) connections to the manifold can be used and a hood arranged over each as before. However, Ochert and Steckelmacher (OS2) recommend that such components are best immersed in the manifold. The manifold must therefore have a series of small demountable chambers connected to it (Fig. 9.2). A component is then placed inside one of these chambers so that its outer surface is exposed to the vacuum, but with the narrow tube connection passing through a cover plate on the chamber. The component is first evacuated via this tube with a rotary pump and then hydrogen or helium (butane is usually undesirable) is admitted to its interior.

If one of the articles under test is found to be leaking badly, it must be sealed or removed to prevent it from interfering with the detection of small leaks in the remaining articles.

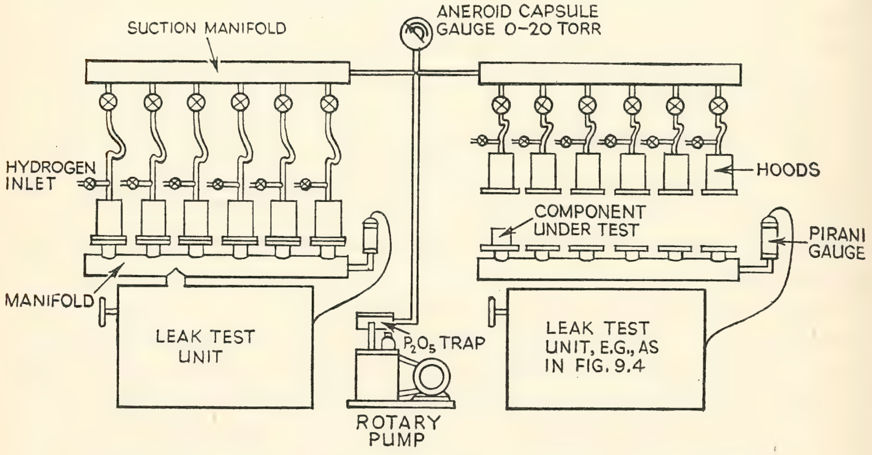


FIG. 9.2 Arrangement of manifolds for leak-testing a number of similar small articles (*after Ochert and Steckelmacher*)

To locate the actual position of the leak, a fine jet of search gas is played over the surface of the apparatus or component under test. This fine jet may be obtained by connecting a drawn-down glass tube via a flexible rubber tube to the reduction valve of a cylinder of the gas; an 'Aerograph' gun is also convenient. When the jet is in the locality of the leak, search gas entering the system produces a response of the leak detector element. In the use of this probing method, Guthrie and Wakerling (GW1) emphasize the following points:

(*i*) Begin with a moderate flow of gas; (*ii*) when a leak detector response is noted reduce the gas flow through the jet; (*iii*) start from the top and work downwards if the search gas is lighter than air; (*iv*) the search gas diffuses rapidly in air, so care must be taken to ensure that the jet is actually at the leak; the temporary isolation of parts of a complex system by means of a piece of cardboard or adhesive tape is often useful.

9.7. The Search Gas Method with a Single Vacuum Gauge

For the pressure range from 10^{-3} to 1 torr, the gauge which has been employed most is the Pirani gauge, but the thermocouple and the thermistor gauge can also be used. These gauges can therefore be employed with a rotary pump alone. The **backing-space technique** in which the gauge is connected to the tubulation or reservoir volume between a vapour pump and the

rotary backing pump is preferred, as then advantage accrues from the compression of the gas between the inlet and outlet of the vapour pump and, moreover, the Pirani gauge can be employed with an inlet-side pressure in the range from 10^{-3} to 10^{-6} torr.

For direct use at pressures less than 5×10^{-3} torr, a hot-cathode or cold-cathode ionization gauge is generally used. The adverse effect on the work function of (and therefore on the electron emission from) a tungsten filament of a diode valve on using oxygen as the search gas has also been used (Lawton, L14; Nelson, N8), but this method is liable to contamination of the thermionic filament by residual gases and vapours present in the vacuum system.

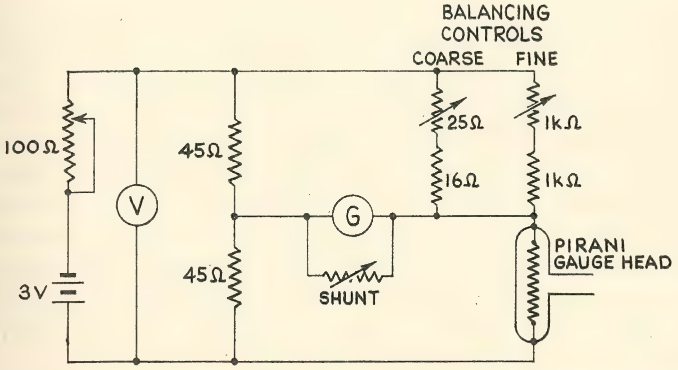


FIG. 9.3 Control circuit for a Pirani gauge adapted for leak detection (*after Ochert and Steckelmacher*)

In the design of special leak-detection plant the use of a single vacuum gauge with a barrier that admits only the search gas (§ 9.8) or the use of two identical vacuum gauges in the differential method (§ 9.9) is much preferred. The simple use of a single gauge therefore applies usually only to leak detection on general vacuum systems.

For routine leak hunting on vacuum systems the use of a Pirani gauge is common practice with butane as the preferred search gas, but where hydrogen is often used, particularly if the speed of the pump cannot be artificially restricted to take advantage of the higher molecular weight of butane (§ 9.5). The simplest procedure is to attach the Pirani gauge to the system which is pumped by a rotary pump. If the gauge indicates a pressure greater than about 10^{-2} torr, a leak is suspected. To carry out the search gas method, the Pirani gauge must then be balanced at the pressure prevailing and a more sensitive indicating meter substituted for the existing panel-mounted instrument. A control circuit for a Pirani gauge (Fig. 9.3) is given by Ochert and Steckelmacher (OS2); similar circuits are built into the commercial Pirani gauges which can be readily adapted for leak detection.

A typical procedure is as follows: the galvanometer shunt resistance is set at a minimum to reduce the galvanometer current sensitivity before switching over to this instrument from the panel-mounted meter (which is usually calibrated in torr in commercial instruments). The coarse balance control is then varied to give a balance, the galvanometer sensitivity increased by increasing the shunt resistance, and the fine balance control is varied. The final setting is made as stable as possible. Without special precautions, it is found that the galvanometer current sensitivity cannot be reduced much below 10 mm/μA as balance drift is experienced.

A jet of search gas is then passed slowly over the surface of the system and should be maintained for some seconds at likely places of leak. On locating the leak, entry of the search gas to displace some of the air in the region of the Pirani gauge will cause a pronounced deflection of the galvanometer spot from the balance at or near zero.

To increase the sensitivity of this method, the pumping speed may be restricted (and variations of this speed reduced) by partially closing the isolation tap between the chamber and the pump. The connection of the Pirani gauge by a tube of low conductance to a ballast volume of one or two litres is recommended by Ochert and Steckelmacher (OS2). To improve the balance stability, and so allow a galvanometer of current sensitivity of 100 mm/μA or more to be used, Blears and Leck (BL2) suggest that a 3 in. thickness of cotton wool be wrapped around the Pirani gauge head to protect it from draughts. A sudden pressure rise of 10^{-6} torr can then just be detected. The use of two balanced Pirani gauge heads (§ 3.6) with their envelopes immersed in liquid air or solid carbon dioxide with acetone leads to a still further improvement of sensitivity.

Without special thermal shielding of a single gauge head, the minimum detectable air leak is about 10^{-5} litre-torr per sec (10^{-2} lusec) if hydrogen is used as the search gas.

If the backing-space technique is employed (Cuykendall, C3) longer search times are necessary but considerably increased sensitivity is attained and the fine-side pressure may be below 10^{-3} torr.

A single hot-cathode ionization gauge with helium as the search gas is reported to be useful and convenient by Dushman (D1). Hydrogen can also be used. Riddiford has stated (discussion on the paper by Blears and Leck, BL2) that at Birmingham University 'we use liquid trichlorethylene probing for all our leak-hunting, with a single ionization gauge'. The current through the tungsten thermionic filament of the gauge is maintained constant. When the trichlorethylene covers a leak, the gauge positive ion current is increased for two reasons: first, the ionization probability for trichlorethylene is much higher than for air; second, this vapour causes a considerably decrease of the work function of tungsten. These additive phenomena result in the gauge being about 25 times as sensitive to trichlorethylene as to air.

According to Blears and Leck, however, butane is the preferred gas for use with an ionization gauge (Table 9.2) because it has a large ionizing cross-section in addition to low viscosity and high molecular weight.

A cold-cathode ionization gauge of the Penning type can be similarly used, the Penning–Nienhuis version of this gauge (§ 3.10) being probably the most satisfactory.

With a single ionization gauge of either the hot- or cold-cathode type, the minimum detectable air leak is about 10^{-6} litre-torr per sec (10^{-3} lusec).

9.8. The Use of a Single Vacuum Gauge with a Barrier that Admits Only the Search Gas

A considerable difficulty in leak detection is that spurious deflections of the vacuum gauge may arise because of virtual leaks in the system and back-streaming of pump fluid. A system which has not been degassed by baking and where no cold-trap is used will usually have a virtual leak of about 10^{-2} litre-torr per sec even after pumping for 10 min or more. Most of the desorbed gas is water vapour so that a phosphorus pentoxide trap between the vacuum system and the gauge effects a considerable improvement.

A useful method of overcoming this difficulty is to arrange between the gauge and the vacuum system a barrier which passes only the search gas. Two techniques of achieving this both use hydrogen as the search gas: the first is the so-called **'charcoal-Pirani method'**, described by Kent (K13) and the second is the use of a heated palladium disc between the gauge and the system, reported originally by Nelson (N9) and now known as the **palladium barrier leak detector.**

Both these methods are primarily intended for the construction of special vacuum plant for leak-detection purposes. In the design of such plant the best practice is to use *two diffusion pumps in series and backed by a rotary pump with the leak detector gauge head connected to the region between the diffusion pumps or to a ballast volume in this region.* This results in an increase in sensitivity of about 30 times or more because gas flow into the inlet side of the first diffusion pump (*i.e.* that connected to the vessel or component under test) accumulates at the gauge head because of the smaller speed of the second (backing) diffusion pump. This accumulation would occur, of course, if only a single diffusion pump backed by a rotary pump were used, but then fluctuations of the speed of the rotary pump and, moreover, evolution of hydrogen from solution in the rotary pump oil, would both lead to spurious fluctuations of the leak detector gauge reading.

The basic layout of the vacuum plant is therefore similar for both these barrier techniques (Fig. 9.4).

The first diffusion pump D_1 is of a speed chosen in relation to the order of size of the vessels to be leak tested. A small plant would employ, for example, a 2 in. port diameter oil diffusion pump with baffle valve whereas a 9 in. pump would be chosen for testing large equipment, say tanks of above 30 litre in volume. This pump is connected via a ballast volume B to a second backing diffusion pump D_2 which is then backed by a rotary pump P of appropriate capacity. It is good practice to provide a by-pass line BL from the rotary pump to the equipment under test as this enables the operating cycles to be faster and also preliminary detection of large leaks at a pressure of about 10^{-2} torr. Isolation valves are necessary as follows: V_1 between the two diffusion pumps, V_2 in the by-pass line to D_1 and V_3 in the line to D_2. Saunders valves (§ 5.11) are often employed.

The charcoal-Pirani method is reported by Kronberger (K7) to be so simple and reliable that it 'has been introduced into most of the vacuum testing installations of the Industrial Group of the United Kingdom Atomic Energy Authority'. The technique depends on the fact that degassed, activated charcoal (§ 6.7) cooled with liquid nitrogen or solid carbon dioxide with acetone will absorb readily atmospheric gases but will absorb hydrogen only slightly. A cooled charcoal trap *T* is therefore inserted in front of a standard Pirani gauge in the connection from the ballast volume *B* (between the diffusion pumps) to this gauge. With this unit, isolation valves V_4 and V_5 are also necessary, one between *B* and *T* and the other between the gauge *G* and the connection of valve V_1 to the second diffusion pump D_2 (shown by dashed lines in Fig. 9.4). The charcoal trap (Fig. 9.5(*a*)) is made from stainless steel tube and is 12 in. long and 1 in. outside diameter. It is filled with 50 gram of degassed activated charcoal. As excess hydrogen pressure may accumulate in this trap if it warms up with valves V_4 and V_5 inadvertently closed, a blow-off valve (Fig. 9.5(*b*)) is attached to it. This valve is simply a metal plug with drilled holes placed in a Wilson seal; if the pressure in the trap becomes excessive, the plug moves out through the Wilson seal until the gas escapes to the atmosphere through the drill-holes.

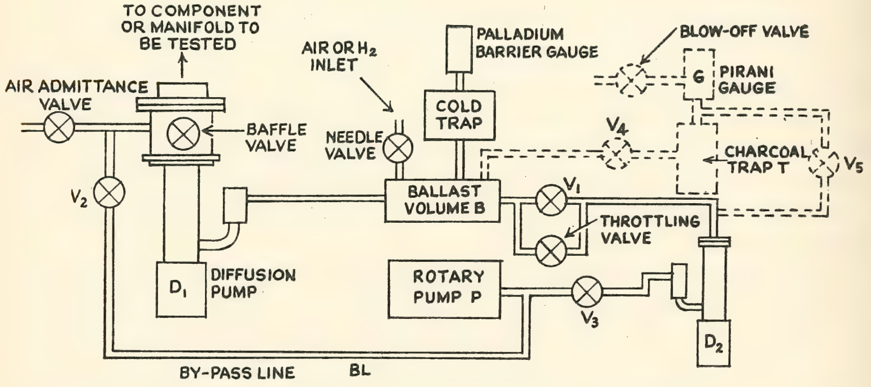


FIG. 9.4 Basic arrangement of vacuum system for leak detection in which a charcoal-Pirani (dashed line connections) or a palladium barrier (full lines) leak detector is used

The standard commercial Pirani gauge employed by Kent used a galvanometer for which a deflection of 14 cm corresponded to a change of air pressure of 10^{-3} torr.

The procedure is to connect the component under test as shown in Fig. 9.4, exhaust it in the usual way by the pumps, cool the charcoal trap by immersing it in liquid nitrogen (or solid carbon dioxide with acetone), close the outlet valve V_5, open the inlet valve V_4 and close the valve V_1 between the pumps. The component is then probed with the search gas or the hood method is used. If a leak is present, a deflection of the Pirani gauge galvanometer is obtained. To determine the size of the leak, a standard leak *L* (§ 9.15) is compared with the component leak. Then, as the method is substantially linear in response:

$$\text{the component leak rate} = \frac{\text{standard leak rate} \times \text{deflection obtained for component}}{\text{deflection obtained for standard leak}}$$

The response to leakage can be varied by altering the conductance of the outlet valve V_5, depending on its throttling. The response is independent of the ratio of the pumping speed to the volume, but the response is more rapid if this ratio is high.

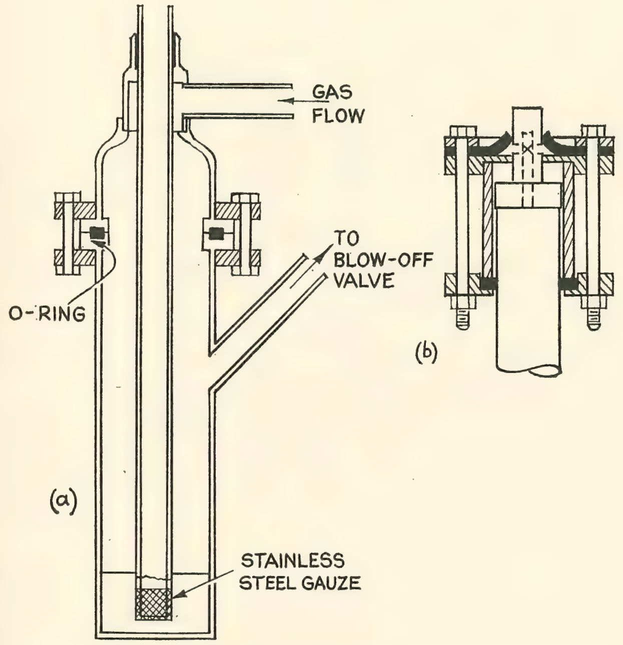


FIG. 9.5 Charcoal trap for the charcoal-Pirani method

As fluctuations of the galvanometer reading (full-scale deflection: 14 cm) are less than 1 mm, a deflection of 5 mm is considered significant corresponding to a minimum detectable air leak of about 4×10^{-7} litre-torr per sec.

The charcoal can be degassed by removing the coolant and heating it to 200° to 300° C under vacuum.

As an alternative to charcoal, silica-gel cooled with liquid nitrogen can be used. It has the advantage over charcoal that the fall in response is more rapid when the search gas is removed from the leak but the disadvantage that it requires more frequent degassing.

Although satisfactory results, but with a slower response, were obtained using this trap and gauge on the fine side of a single diffusion pump, this method was found to give poor results if used with a mechanical rotary pump alone because of the larger pressure fluctuations obtained and the necessity for working at a higher pressure.

The palladium barrier leak detector was invented by Nelson (N9) and first marketed by the Radio Corporation of America as the special type of triode ionization gauge R.C.A. 1945. A British model is produced by Edwards High Vacuum Ltd., the essential features of which are shown in Fig. 9.6 (after Ochert and Steckelmacher, OS2). It is a triode ionization gauge within a glass envelope (a metal envelope is used in the R.C.A. model) of which the essential electrodes are a thermionic cathode, a palladium disc sealed over the end of a Kovar tube as the anode and a cylindrical positive ion collector. This device is sealed off under vacuum and gettered. The ion collector also acts as a focusing device for the electrons emitted from the plane cathode so that they are concentrated on to the surface of the palladium disc. This electron bombardment heats the disc up to about 800° C, with an anode dissipation of 6 W, when it becomes permeable to hydrogen but not to other gases. When hydrogen is admitted through the palladium barrier the positive ion current in the gauge head is increased above the background value due to the small residual gas pressure of about 10^{-7} torr. The ionization current is amplified

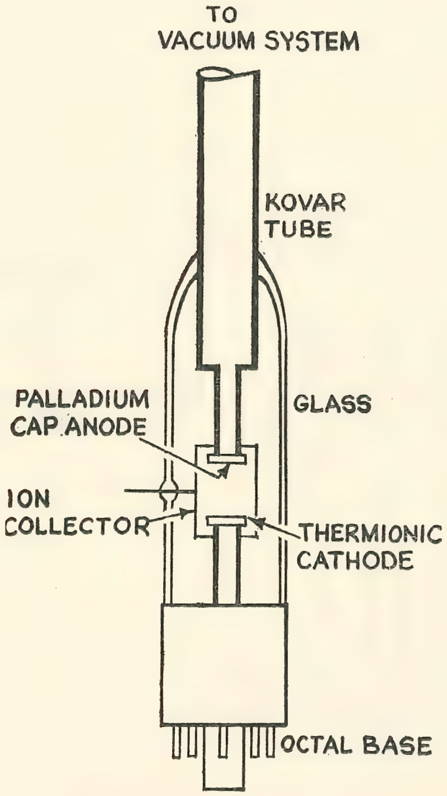


FIG. 9.6 Construction of the palladium barrier gauge head

by a d.c. amplifier (or a vibrating reed electrometer) with a current gain of about 10^5.

An electrical circuit for operating this palladium barrier gauge head is given by Ochert and Steckelmacher (OS2); a slightly modified version of this is shown in Fig. 9.7.

This palladium barrier gauge is connected via a cold-trap to the ballast volume B between the diffusion pumps D_1 and D_2 (Fig. 9.4).

Difficulties of this method and remedies suggested (Ochert and Steckelmacher, OS2) are as follows:

(*i*) Hydrocarbons from the pump oil and water vapour are dissociated at the hot palladium to produce hydrogen, leading to a spurious response. The cold-trap containing liquid air or solid carbon dioxide with acetone is therefore interposed in the tubulation to the gauge head to freeze out these vapours.

(*ii*) The presence of air in the system results in catalytic oxidation of the hydrogen in the presence of heated palladium. To avoid this difficulty the usual procedure is first to detect (*e.g.* by a Pirani gauge) larger air leaks and seal them before proceeding to find the small ones.

(*iii*) Oxygen absorbed on the palladium may restrict the diffusion of hydrogen; this effect may be reduced by admitting a controlled amount of hydrogen (*e.g.* via a needle valve connected to the ballast volume B, or by heating a Nichrome filament in the system to about 1000° C to decompose oil vapour) if the background amount of this gas is inadequate.

(*iv*) Probably the use of mercury diffusion pumps might give greater sensitivity than oil diffusion pumps, as the latter evolve to a small extent hydrogen from solution in the oil; however, the small fluctuations due to this cause may be balanced out.

9.9. Differential Methods of Leak Detection

The purpose of the differential method is to provide a leak detector which is insensitive to fluctuations of the residual gas pressure (due primarily to variations of pumping speed) in the vacuum system but which is sensitive to displacement of residual air by the search gas in the neighbourhood of the detecting element. This is achieved by the use of two similar gauges connected in an electrical circuit so that the difference between their readings is registered. Both these gauges record the residual permanent gas pressure in the system, but only one of them has a trap which is selective for the probe gas.

The method has been used with Pirani gauges, hot-cathode ionization gauges and Penning gauges. It was first reported by Jacobs and Zuhr (JZ1) who used similar Pirani gauges which were arranged in the adjacent arms of a Wheatstone network so that their resistances were equal when they were both attached to the same point in the vacuum system and were at the same gas pressure, the galvanometer reading being zero. One of the Pirani gauges was connected directly to the system and the other via a liquid-air trap. A

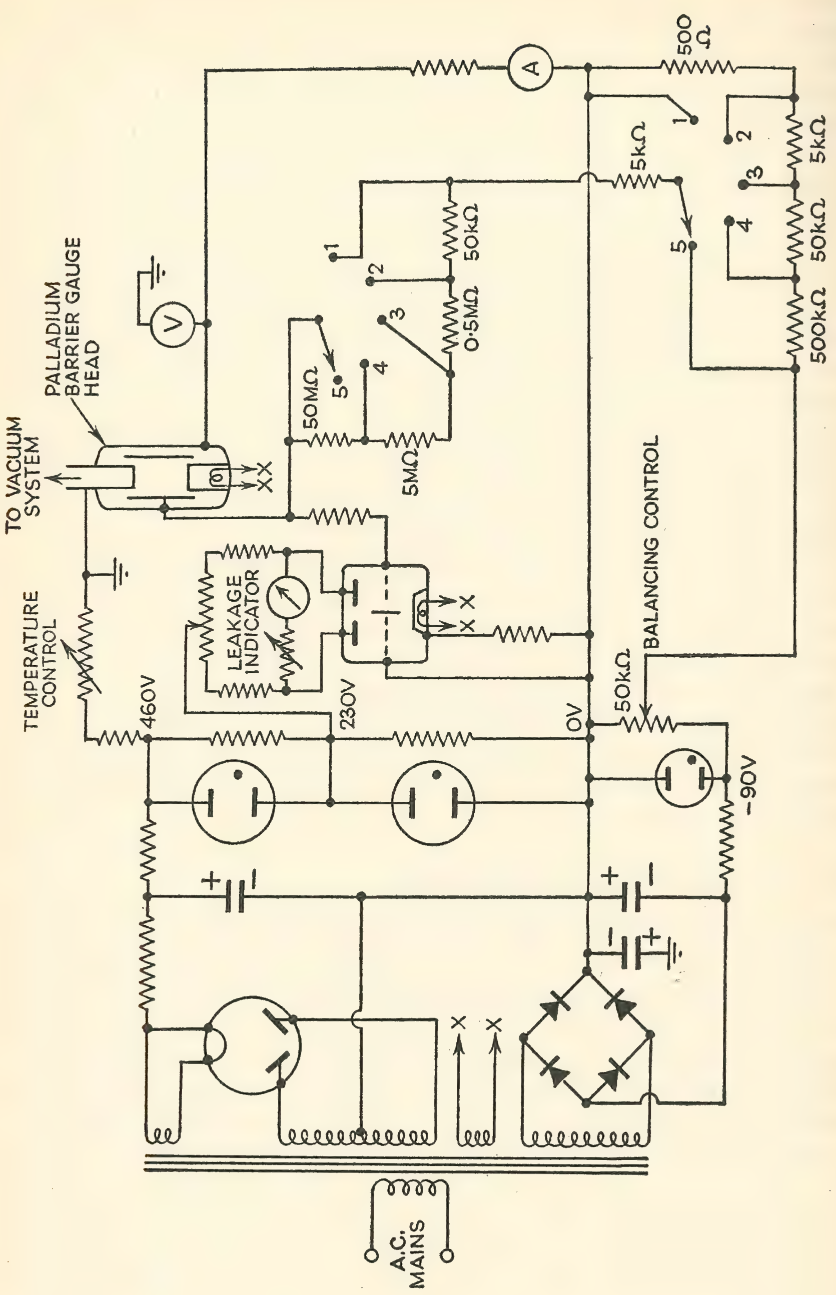


FIG. 9.7 Basic electrical circuit for a palladium barrier gauge head (*after Ochert and Steckelmacher*)

condensable search gas in the form of a hydrocarbon vapour was used; when this covered a leak in the system, the pressure in the trapped gauge decreased, whereas that in the untrapped gauge remained almost constant. The bridge circuit was therefore put out of balance and a deflection of the galvanometer noted.

The principles involved are illustrated by Fig. 9.8. G_1 and G_2 are two similar gauges connected by tubulations T_1 and T_2 respectively to the same location O in the connection to the pumping system. The tubulation T_1 includes a trap A for the search gas (this is not necessarily a cold-trap). To obtain maximum response of the leak detector, the search gas used should have good coverage of the leak, high vapour pressure (preferably above atmospheric pressure), low viscosity and high molecular weight (*see* § 9.5). To ensure that the pressure in gauge G_2 is not lowered appreciably when condensation of the search gas takes place in the trap A, the conductance of the tubulation to G_1 must not be greater than the effective pumping speed for air at O. Also, as the pressure varies at point O, the partial pressure of air in the two gauges must be the same; hence the gauge gas flow-time constants must be equal (Blears and Leck, BL3). To achieve this equality, V_1/U_a' must equal V_2/U_a'' where V_1 and V_2 are the volumes of gauges G_1 and G_2, respectively, and U_a' and U_a'' are the conductances to air of the tubulations between G_1 and O and G_2 and O respectively. As the gauges are similar, this is best arranged in practice by making the conductances and the volumes (including that of the tubulation between the gauges and O) equal.

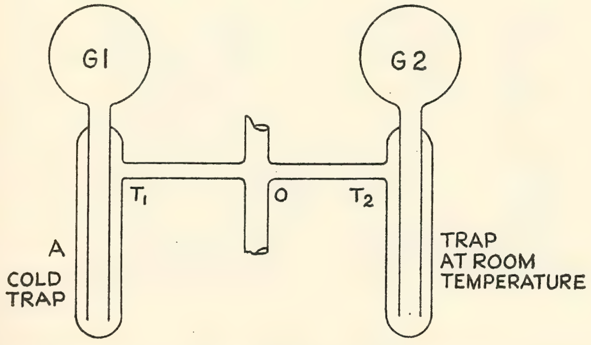


FIG. 9.8 Basic connections used in the differential method

A suitable bridge circuit for differentially connected Pirani gauges is shown in Fig. 9.9(*a*), whilst an arrangement for the connection of hot-cathode ionization gauges is conveniently based on a twin-triode d.c. amplifier (Fig. 9.9(*b*)). Butane as the probe gas gives the best sensitivity if a liquid-air trap is used.

Blears and Leck (BL3) describe a convenient method which uses carbon dioxide (non-inflammable) as the search gas and where the trap contains calcium hydroxide (which absorbs CO_2) at room temperature instead of being cooled by liquid air. They use this technique both with Pirani gauges and with hot-cathode ionization gauges. The metal-cased gauges were conveniently

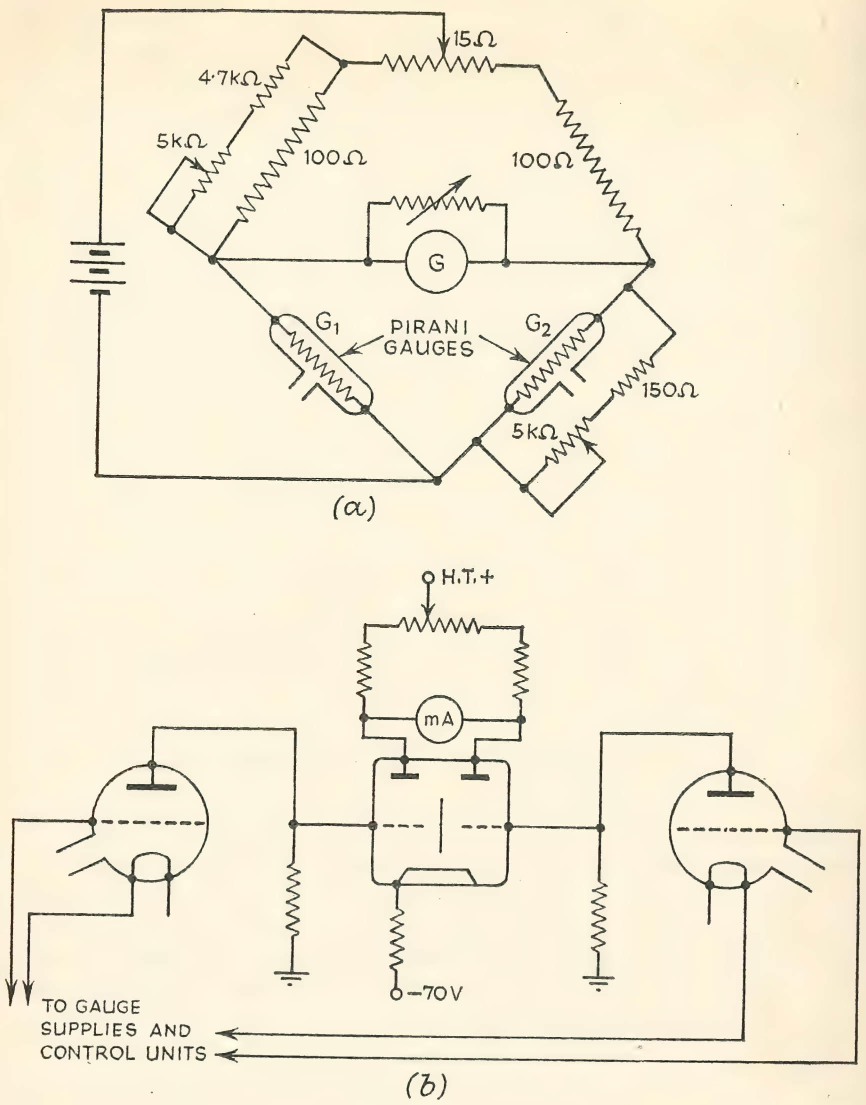


FIG. 9.9

(*a*) Bridge circuit for the differential Pirani method
(*b*) Basic circuit for the differential hot-cathode ionization gauge method

mounted on a union bored out of brass block and which included the absorbent (Fig. 9.10); the symmetry of this arrangement provided the equality of gauge gas flow necessary.

In their investigations of the differential method, Blears and Leck used differentially connected ionization gauges attached to a fine-side chamber pumped by an oil diffusion pump which was backed by a second oil diffusion pump and finally a rotary pump; differential Pirani gauges were connected to the tubulation between the two diffusion pumps. With a 2 in., 3 in. or 8 in.

diffusion pump in the first stage, gas pressure fluctuations were about 2% of the mean gas pressure. As the effect of these fluctuations could be reduced by restricting the conductances of the gauge tubulations, U_a' and U_a'', these were arranged so that the gauge gas flow time constants, V_1/U_a' and V_2/U_a'', were equal and each 5 sec. With the added advantage of differential connection, the apparent pressure fluctuation was reduced to 2·5% of its actual value, *i.e.* to about 0·05% of the mean gas pressure. At very low pressures, however, a limit was set by the inherent instabilities of the gauges themselves and their control circuits. Equivalent pressure fluctuations due to these instabilities were about 10^{-6} torr for the Pirani gauge and 2×10^{-10} torr for the hot-cathode ionization gauge, indicating that the differential ionization gauge method can be used at pressures as much as 5000 times lower than is possible with differential Pirani gauges.

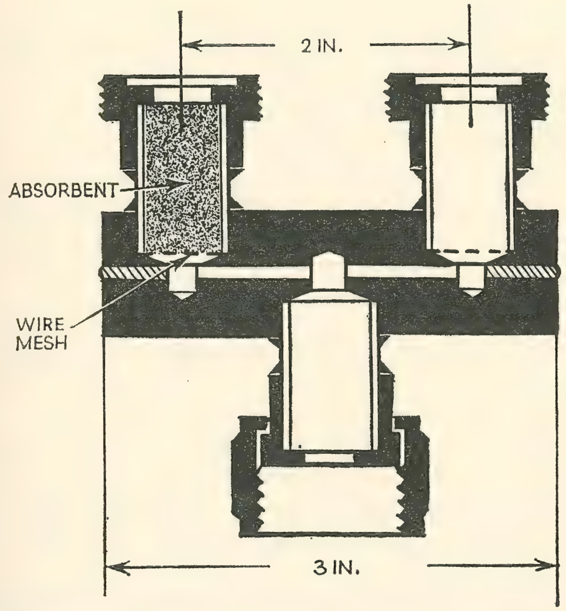


FIG. 9.10 Gauge mounting for the differential method with calcium hydroxide absorbent (*after Blears and Leck*)

In the design of leak-detection plant using the differential method, Blears and Leck recommend the use of ionization gauges on the fine side and a diffusion pump with an isolation valve that can be throttled so that the overall time constant of the system is 5 sec. The use of Pirani gauges is preferred for a range of intermediate leak sizes and especially where the operator is unskilled. To attain sensitivity with Pirani gauges the pressure must be increased to about 10^{-3} and hence, for small leaks, the backing space technique, *i.e.* Pirani gauges between two diffusion pumps, is necessary. If the volume of the backing space between these pumps is kept small the conductance of the corresponding backing line can be so restricted that a compression ratio of

250 between the fine side and backing side volumes of the first diffusion pump is possible, without the time constant exceeding 5 sec. With carbon dioxide as the probe gas and a calcium hydroxide trap to one of the differential gauges, a minimum detectable leak of 10^{-6} litre-torr per sec can be achieved.

As the absorbing power of calcium hydroxide for carbon dioxide falls off with time, it should be changed about once a month. Kronberger (K7) alleges that absorption of impurities on the calcium hydroxide causes difficulty in some vacuum operations.

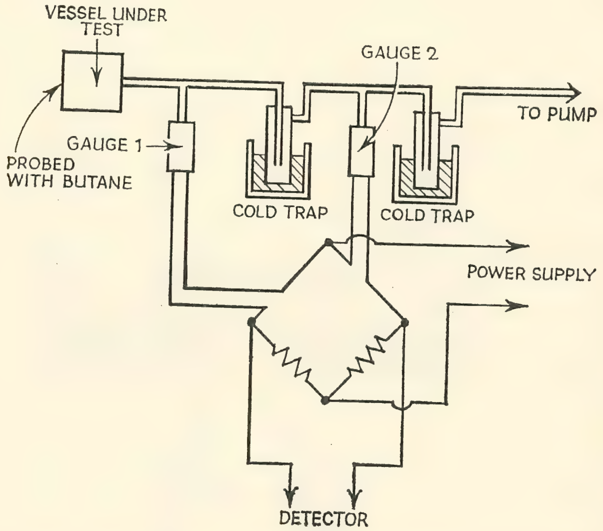


FIG. 9.11 Leak detection plant using differential cold-cathode ionization gauges (*after Lundberg*)

Lundberg (L15) has designed a leak detector using differentially connected cold-cathode ionization gauges of the Klemperer type (§ 3.10), preferred because there is no filament to burn out, and the maximum pressure recordable is 10^{-2} torr instead of 10^{-3} torr with the hot-cathode gauge. Butane was used as the search gas. The plant was developed for the location of very small leaks in metal-to-glass seals in the production of television cathode-ray tubes. It has the gauges connected to the fine side of a mercury diffusion pump with liquid-air trap (Fig. 9.11), an auxiliary liquid-air trap being connected in front of one of the gauges to condense out the butane. Full details of the bridge circuit are given in Lundberg's paper, which includes switching to increase the p.d. across the gauges to degas them by electron bombardment. The response time of this leak detector plant was 5 to 10 sec and it is claimed to locate leaks of the order of size of 1 to 0·1 litre micron per hour, *i.e.* $2{\cdot}8 \times 10^{-7}$ to $2{\cdot}8 \times 10^{-8}$ litre-torr per sec.

Beck and King (BK1) have also developed leak detection plant using differentially connected cold-cathode ionization gauges of the magnetron type described by Beck and Brisbane (§ 3.10). As difficulties were experienced with d.c. amplification, the bridge circuit designed included gauges of which the current was modulated at audio-frequency (700 c/s). To achieve this modulation the magnetron gauges were each operated in the combined magnetic fields produced by a solenoid carrying d.c. and an auxiliary helical coil supplied with a.c. at 700 c/s (Fig. 9.12(*a*)). The magnitude of the constant magnetic field was chosen so that each gauge operated on the steep part of the curve of the gauge current against magnetic field. With the alternating magnetic field on, the a.c. component of the gauge current produced an alternating p.d. across the gauge cathode load resistor; to compare the alternating signals from the two gauges they were made the input to a differential amplifier. Full details of the electrical circuits used are given in the original paper.

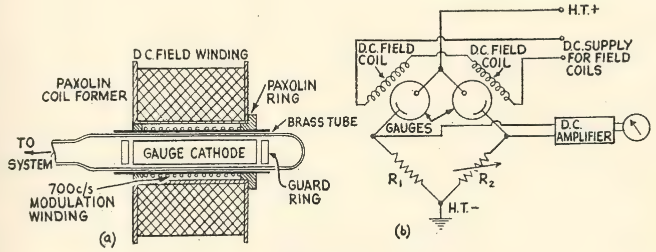


FIG. 9.12

(*a*) The magnetron cold-cathode gauge and associated field coils
(*b*) Basic circuit diagram of the bridge circuit used by Beck and King

The vacuum system had two mercury diffusion pumps in series with a rotary backing pump. It was found that mercury pumps, when adjusted to boil steadily, gave smaller pumping speed fluctuations than did oil diffusion pumps. The differential gauges were connected to the fine-side volume with a liquid-air trap between them to condense the butane used as a search gas. An Alpert valve (§ 5.9) connected in the tubulation from the gauges to the diffusion pump acted as a fine control of the pumping speed. To reduce mechanical vibration at the gauges, the rotary pump was mounted on shock absorbers and a rubber hose was included in the backing line to the rotary pump. This unit is claimed to detect air leaks as small as 10^{-10} litre-torr per sec.

Mass Spectrometer Leak Detectors

9.10. The Use of Magnetic Deflection Mass Spectrometers (*cf* § 3.12)

The most sensitive, most reliable but most expensive way of constructing leak-detection plant is to use a magnetic deflection mass spectrometer with helium as the search gas.

Early investigators of this technique were Worcester and Doughty (WD1), Nier, Stevens, Hustrulid and Abbott (NSHA1) and Thomas, Williams and Hipple (TWH1). The first two teams used a 60° deflection instrument with a sector magnetic field provided by a permanent magnet; the third team designed a 180° instrument. The mass spectrometer of Worcester and his colleague has a sector magnetic field strength of 900 gauss and an ion accelerating potential of 270 V so that the radius of curvature for singly charged helium ions is 5·25 cm (*see* equation 3.17). The outlet slit to the ion collector in relation to the other defining slits is set to establish this radius so that only helium ions reach the collector; other gaseous ions present are deflected to one side or other of the slit. An oil diffusion pump with cold-trap (filled with solid carbon dioxide and acetone) backed by a mechanical rotary pump is used to evacuate this instrument, the pumping speed being about 30 litre per sec (Fig. 9.13(*a*)). The plant, chamber or tube under test (*see* arrangements described in § 9.6) need be pumped only to a backing pressure (10^{-2} to 10^{-3} torr) provided that a needle valve inserted in the tubulation to the mass spectrometer is adjusted to prevent pressure increases in this instrument to above 5×10^{-4} torr. Helium probing or a helium hood test is then applied. The mass spectrometer built by Nier *et al.* (*see* Fig. 9.13(*b*)) has a central ion beam radius of 2 in. Baffles inserted between the ion source and the analyser

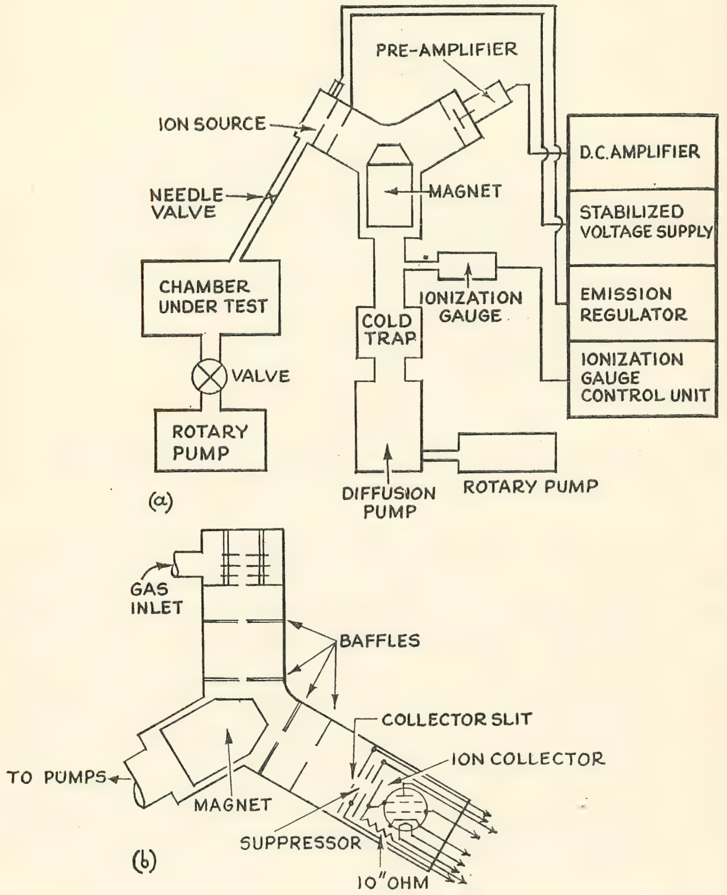

PRE-AMPLIFIER
ION SOURCE
NEEDLE VALVE
MAGNET
D.C. AMPLIFIER
STABILIZED VOLTAGE SUPPLY
CHAMBER UNDER TEST
COLD TRAP
IONIZATION GAUGE
EMISSION REGULATOR
IONIZATION GAUGE CONTROL UNIT
VALVE
ROTARY PUMP
DIFFUSION PUMP
ROTARY PUMP
(a)
GAS INLET
BAFFLES
COLLECTOR SLIT
ION COLLECTOR
TO PUMPS
MAGNET
SUPPRESSOR
10''OHM
(b)

FIG. 9.13 Arrangement of mass spectrometer leak detector

region are to ensure a higher gas pressure in the source (and hence effective production of ions by electron impact) than in the remainder of the mass spectrometer tube. The 180° mass spectrometer of Thomas *et al.* has an external Alnico permanent magnet to produce a field of about 1540 gauss and an ion accelerating potential of 350 volt giving a radius of curvature for helium ions of 3·5 cm.

With these instruments about 1 part of helium in 4×10^5 parts of air can be detected at the optimum. Jacobs and Zuhr (JZ1) report the minimum detectable air leak to be between 8×10^{-8} and $1{\cdot}6 \times 10^{-7}$ litre-torr per sec for a vessel of volume between 1 and 10 cu ft. For an increase of volume by a factor of n, the minimum leak detectable is roughly n times smaller.

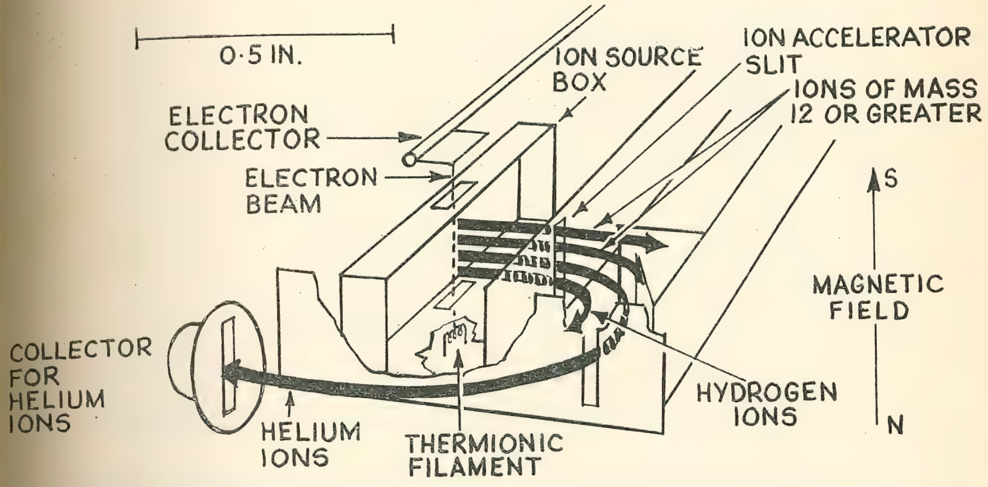

0·5 IN.
ION SOURCE BOX
ION ACCELERATOR SLIT
IONS OF MASS 12 OR GREATER
ELECTRON COLLECTOR
ELECTRON BEAM
S
MAGNETIC FIELD
N
COLLECTOR FOR HELIUM IONS
HELIUM IONS
THERMIONIC FILAMENT
HYDROGEN IONS

FIG. 9.14 Outline of the diatron

The A.E.I. (Manchester) mass spectrometer leak detector, type MS6L, is a 90° instrument with a 10 cm radius central ion path and is reported to record a minimum detectable leak of 5×10^{-10} litre-torr per sec. As helium is expensive, three versions of this instrument are available using magnets with different field strengths: (*i*) for use with helium has a mass range from 4 to 32; (*ii*) uses methane (in coal gas) as the search gas and the mass range 14 to 56; (*iii*) is for use with argon or butane and the mass range 30 to 120. Roughly, the sensitivity is 10 times greater if helium is used compared with the other, cheaper search gases. The maximum resolving power is 80, exceeding considerably that required. An audible alarm ('squealer') can be adapted to give a warning of the presence of a leak so that the operator need not keep the output meter under continual observation.

A miniature 180° mass spectrometer known as the *Diatron* is manufactured by the Consolidated Electrodynamics Corporation, U.S.A. (Fig. 9.14). Charpentier (C4) gives details of the circuits of the power supply, ion current amplifier and filament emission regulator (involving all together only six thermionic valves) for this instrument. The minimum detectable air leak is reported to be 10^{-8} atmosphere cm^3 per sec, *i.e.* $7{\cdot}6 \times 10^{-9}$ litre-torr per sec.

Peters and Raible (PR1) have designed an ion source for a mass spectrometer in which the repeller electrode is in the form of a flat grid which is heated by the direct passage of electric current to 1000° C (Fig. 9.15). This prevents the formation of deleterious films on the source electrodes which tend to accumulate as a result of back-streaming of the diffusion pump oil. According to these authors, the usual mass spectrometer ion source needs to be cleaned about once a week to retain maximum sensitivity whereas this new heatable ion source can be operated continuously for as long as a year without maintenance. Raible (R18) describes an automatic leak-testing station incorporating an ion source of this type able to test small components such as electron tubes at a rate exceeding 200 articles per hour.

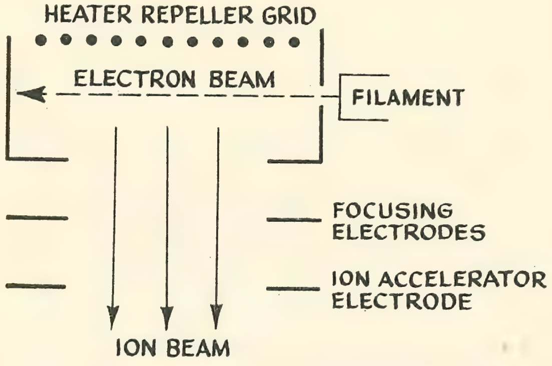


FIG. 9.15 Ion source with heated repeller electrode (*after Peters and Raible*)

The use of hydrogen is attractive on the score of economy in place of helium as a search gas. However, difficulty in using hydrogen is experienced as the background mass spectrum normally exhibits hydrogen due, for instance, to cracked pump oil molecules in the vacuum chamber and due to virtual leaks (*see* Fig. 3.33). Edwards High Vacuum Ltd. have introduced recently a new type of mass spectrometer in which the positive ions are focused on to the ion collector by an axially symmetrical magnetic lens. The central ion beam follows a linear path and is not deflected through an angle as in a sector field instrument. It can be used with helium but has been designed particularly for use with hydrogen as the search gas. The background ion current due to hydrogen is reported to be so low, even when testing components with a virtual leak, that a minimum detectable air leak of 5×10^{-10} litre-torr per sec is recordable.

The use of a Nier mass spectrometer with an electron multiplier to measure the positive ion currents (§ 3.12) enables a leak detection system of the highest sensitivity achieved so far to be constructed. Warmoltz and Grefte (WG1) describe such an arrangement based on a 5 cm radius Nier mass spectrometer with a modulated ion source which is able to detect a minimum leak of 10^{-12} cc-S.T.P. per sec, *i.e.* $1{\cdot}3 \times 10^{-12}$ litre-torr per sec in 2 sec and $6{\cdot}6 \times 10^{-14}$ litre-torr per sec if the isolation valve to the pump is closed so that the gas is allowed to accumulate for 10 sec. This very high sensitivity enables an air–helium mixture containing 1% helium to be used as a cheap search gas yet with a minimum detectable leak about five times that recordable if a conventional mass spectrometer with pure helium is used. This development is of considerable value in the testing of electron tubes for very small leaks which may cause an undesirable residual pressure increase over long periods (*see* § 9.1).

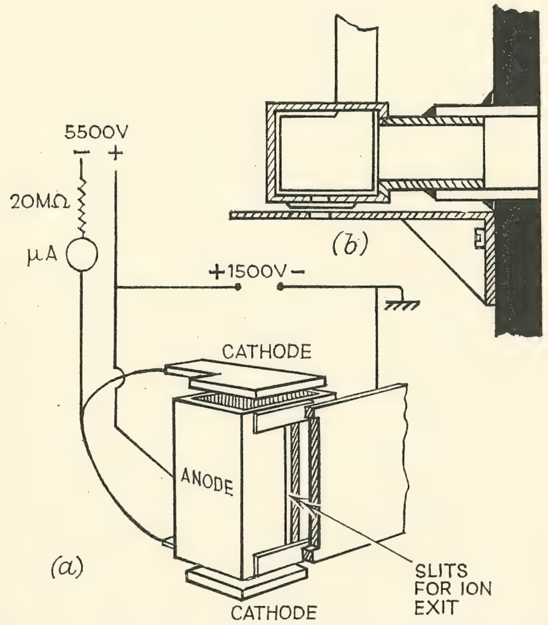


FIG. 9.16 Cold-cathode ion source for mass spectrometer

(*a*) Cut away perspective view
(*b*) Mid-section perpendicular to magnetic field (*after Milner*)

The thermionic filament of a hot-cathode ion source is liable to burn out, must have a regulated heater current for good leak detection sensitivity and restricts the maximum pressure at which the mass spectrometer can be safely operated to about 5×10^{-4} to 10^{-3} torr. Furthermore, a cold trap is necessary in the pumping system. Even so the life is limited. These difficulties are avoided if a cold-cathode ion source is used (§ 3.12). The resolving power possible is then restricted because of the energy spread amongst the emitted ions, but this is not serious as adequate resolution at low mass numbers for leak-detection purposes is possible. The more noteworthy limitation applies to the detection of small leaks at low gas pressures; if the pressure in the ion source is too small it is difficult to ensure an adequate supply of ions. Guthrie and Wakerling (GW1) and Milner (M4) both describe Penning gauge type cold-cathode ion sources for use in a leak-detector mass spectrometer. The Milner design (marketed by the Associated Electrical Industries (Rugby) Ltd.) is an 180° instrument with a 4·5 cm radius. The ion source electrode system (Fig. 9.16) is conveniently mounted on a removable face plate and inserted into a flat-sided rectangular metal chamber within a U-shaped magnet. The cathodes of the ion source are at −5500 V with respect to the anode. The ion energy spread is 3 to 5% at 1500 V, the subsequent ion accelerating potential used. As multiply charged ions are produced in such ion sources to a greater extent than in controlled hot-cathode ones, a considerable background appears at mass number 4 (*e.g.* due to N^{+3} at $14/3 = 4\frac{2}{3}$, though experimentally the background appears to be due to polyatomic ions due to dissociated pump oil vapour, reported to be less noticeable with silicone oil than with Apiezon oil). It is essential that the helium used as search gas produces a peak in the mass spectrum which is readily identifiable against this background. In this respect, considerable improvement results if the ion beam velocity is modulated at 50 c/s, so that the beam of helium ions are swept backwards and forwards across the collector slit. As this produces 100 ion pulses per sec, the subsequent amplification is by an a.c. amplifier tuned to 100 c/s. The minimum detectable air leak is 10^{-8} litre-torr per sec.

Though a convenient rugged design requiring little servicing, sufficient ions are not produced in the ion source unless the pressure there is greater than 10^{-4} torr. As the instrument may be expected to detect 1 part of helium in 4×10^5 parts of air, this means that partial pressures of helium less than $2{\cdot}5 \times 10^{-10}$ torr cannot be detected whereas the hot-cathode instruments are able to register such partial pressures as low as 10^{-11} torr. Thus, the use of a hot-cathode gives intrinsically 10 to 100 times greater sensitivity. Moreover, the Milner mass spectrometer used an electromagnet weighing 50 kg; the same resolving power could be achieved in a small radius hot-cathode instrument with a permanent magnet weighing only about 1 kg. The cold-cathode mass spectrometer is, however, especially suitable when the gas and/or vapour output from the vessel under test is large and where a cold-trap is not used on the spectrometer pumping system.

9.11. The Use of Time-of-flight Mass Spectrometers

A simple design of radio-frequency mass spectrometer (§ 3.13) for leak detection (Fig. 9.17(*a*)) has been designed by Váradi and Sebestyén (VS1). Using hydrogen or helium as the search gas a small mass resolving power is adequate; it was only about five for hydrogen. This permits a source which does not give monoenergetic ions. It consisted simply of a heated tungsten filament *F* giving an emission current of 5 mA and grid G_1 at +150 V with respect to *F*. Grids G_2, G_3 and G_4 form the analyser; these are at a steady potential of −50 V with respect to the filament *F* with a superimposed r.f. voltage of 15 V r.m.s on grids G_2 and G_4. Grid G_5 is at +150 to +190 V with respect to *F* and forms a retarding barrier for positive ions. The collector electrode *C* is at −50 V relative to *F*. The grids are spaced at 7 mm from each other and are each wound with twenty loops of 0·03-dia tungsten wire on a circular nickel wire frame of diameter 18 mm; they are mounted on glass rod supports. The grids near the cathode are gold-plated. The overall size of the containing glass envelope is only 7 cm long by 3·5 cm dia.

A simple electronic circuit is used to stabilize the filament emission against line voltage changes and variations of the gas pressure in the tube. This circuit also includes a relay to break the filament circuit if the pressure in the tube rises too much. The ion current to *C* is measured by a feedback d.c. amplifier (Fig. 9.17(*b*)) and a conventional valve oscillator is used to provide the r.f. supply with a peak voltage of 15 V. With the given d.c. potentials, the frequency is 7 Mc/s for hydrogen. Using hydrogen as the search gas, the minimum detectable air leak is $2{\cdot}8 \times 10^{-8}$ litre-torr per sec, the ratio of minimum detectable hydrogen to residual gas pressure being about 1 to 10^4.

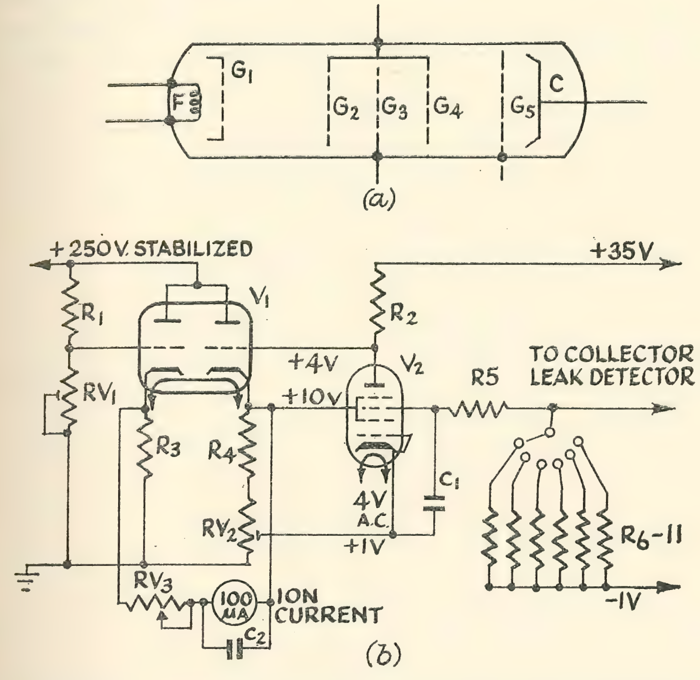


FIG. 9.17 R.F. mass spectrometer leak detector (*after Váradi and Sebestyén*)
In (*b*) $R_1 = 0{\cdot}12$ MΩ; $R_2 = 5$ MΩ; $R_3 = 4$ kΩ; $R_4 = 3$ kΩ; $R_5 = 0{\cdot}1$ MΩ; $R_6 - R_{11} = 3 \times 10^8$ Ω. $C_1 = 100$ pF; $C_2 = 1$ μF. V_1 = ECC40; V_2 = 6BE6

Beckman Instruments Incorporated have developed a radio frequency mass spectrometer leak detector (Moody, M13) of a more advanced design able to detect 1 part of helium in 10^6 parts of residual gas.

The use of the omegatron in leak detection is discussed by Bell (B28); the vacuum system used (Fig. 9.18) is designed to detect very small leaks at total pressures not greater than 10^{-6} torr in electron tubes. As a system of small volume which can be baked-out is provided, the method is useful for studies in the ultra-high vacuum range (pressures less than 10^{-7} torr). A mercury diffusion pump with two liquid-air traps is used, the isolation valve being of the greaseless glass type (§ 5.10). A liquid-air trap *T* is connected between the omegatron and the isolation valve. The pressure in the tube under test is monitored by an ionization gauge; this tube and gauge are separated from the omegatron by the trap *T*. The tube, omegatron, gauge, trap *T* and the glass isolation valve can be baked-out at 450° C; on cooling and filling the trap *T* with liquid air the total pressure with the isolation valve closed can be maintained below 10^{-7} torr. For a total residual pressure not greater than 10^{-6} torr, a partial pressure due to helium (used as the search gas) of 10^{-10} torr can be recorded, corresponding to a concentration of 1 part in 10^4. If the system is pumped at a speed of 10 litre per sec, the minimum detectable leak is then 10^{-9} litre-torr per sec, which is similar to that attainable with a conventional magnetic deflection mass spectrometer. However, with the facility for bake-out provided, the maximum outgassing rate can be reduced to such a low value that the isolation valve may be closed for, say, one hour. For a cut-off volume of 0·3 litre, a detectable signal is then possible due to the accumulation of helium which has infiltrated through a leak as small as 10^{-14} litre-torr per sec, comparable with the rate at which helium permeates the glass walls (§ 8.3). Bell reports that, in practice, leaks of the order of 10^{-9} litre-torr per sec are immediately obvious and that smaller leaks of 10^{-10} and 10^{-11} litre-torr per sec have been found; below these values it is difficult to provide a known calibrated leak. Stark (S24) reports that the minimum detectable leak is 4×10^{-11} litre-torr per sec with the omegatron and that by using the accumulation technique this figure may be reduced to about 2×10^{-14} litre-torr per sec. The Elliott Leak Detector Unit (Leybold–Elliott Ltd.) comprises an omegatron head, a Broad cold-cathode ionization gauge (§ 3.10) and an ionization gauge of the Bayard–Alpert type; a stainless steel pump system is used. The Broad gauge is used for the detection

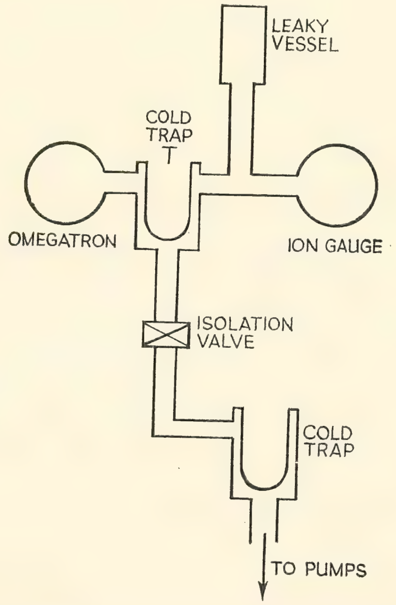


FIG. 9.18 Leak detection plant utilizing an omegatron (*after Bell*)

of large leaks using acetone as the search gas; at a pressure less than 10^{-5} torr, the Bayard–Alpert gauge is used with oxygen as the search gas, the minimum detectable leak being 10^{-9} litre-torr per sec; below this minimum, the omegatron is used and for the maximum sensitivity the accumulation technique is adopted. A heating jacket is provided for baking out the article under test and the Bayard–Alpert gauge, and a separate heating jacket is provided for the omegatron head.

9.12. The Halogen Leak Detector

A versatile leak detector which cannot be classified as either a vacuum gauge device or as a gas analyser depends upon the influence on the positive ion emission from a heated platinum anode of the presence of gas molecules containing one or more of the halogen elements: chlorine, bromine, fluorine and iodine. This instrument, first introduced by White and Hickey (WH1), consists basically (Fig. 9.19(*a*)) of two coaxial cylindrical electrodes in air of which the inner one is an anode made of platinum and is heated to about 900° C by an internal, insulated platinum filament, and the outer one is the cathode, the assembly being mounted in a vacuum-tight container. A p.d. of 50 to 500 V is maintained across these electrodes, a microammeter or a d.c. amplifier for recording the positive ion emission current being included in series with the voltage supply.

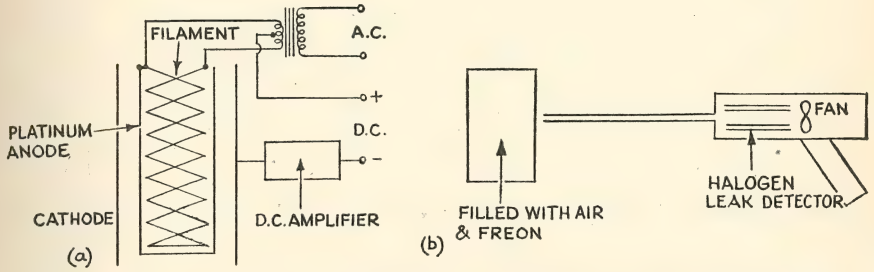


FIG. 9.19 The hot-platinum halogen leak detector

Suitable search gases containing halogens in their molecules are freon 12, carbon tetrachloride, chloroform and trichlorethylene, the first of these being preferred. The halogen sensitive head may be employed in two ways: (*a*) it is connected to a vacuum system (best between the vapour pump and the backing pump) and the surface of the system explored with a probe of the search gas in the usual way; (*b*) the vessel, article or plant is filled with air containing the search gas at a pressure above atmospheric and the outside surface explored with the detector; search gas issuing through a leak to the atmosphere then enters a tube connected to the detector; this is known as the 'sniffer' method (Fig. 9.19(*b*)).

On entering the detector, the presence of the halogen at the heated anode surface increases the positive ion emission from the platinum. An increase of the emission current is therefore recorded. Method (*a*) enables a minimum detectable leak of 10^{-8} litre-torr per sec to be recorded; method (*b*) is considerably less sensitive but can be applied to leak location in other than vacuum plant, *e.g.* in tests on refrigeration apparatus.

A partial pressure of 10^{-8} torr can be detected independently of the total pressure. However, Torney (T4), in a description of the National Research Corporation (N.R.C.) instrument, points out that the background current has a marked influenced on the sensitivity of the detector element; though the sensitivity increases rapidly as the total pressure is decreased to less than 0·2 torr, the background current increases more rapidly than the signal due to halogen admission; the signal-noise ratio is found experimentally to be a maximum in the pressure region between 0·07 and 0·2 torr. For the N.R.C. halogen leak detector the background current is 15 to 40 μA in this pressure range for an anode heater current of 1·6 to 1·9 amp. In use, the element ages and the heater current must be increased to restore full sensitivity. This instrument (Fig. 9.20(*a*)) has an inlet for a clean air supply used to decontaminate the element of halogens and to serve as a pressure regulator to obtain the optimum operating pressure for maximum signal/noise ratio. The basic circuit used (Fig. 9.20(*b*)) was designed to reject the slowly varying background current but to amplify by about 100 times the more rapidly changing signals due to halogen inlet through a leak. To do this, the input circuit to the amplifier consists of a load resistor R_1, across which the signal voltage is developed by the positive ion current, followed by the resistor R_2, capacitor C_1 and diode D, forming, in effect, a filter which passes the band of frequencies in which the required signal lies. High-frequency noise signals from the detector element are by-passed by the capacitor C_2. The two-stage amplifier provides a gain of 100, the output being recorded by a meter, and also drives a thyratron relaxation oscillator of which the audible note (a loudspeaker is used) varies in pitch as the signal due to the leak increases. The minimum detectable leak is stated to be 2×10^{-8} cc-S.T.P. per sec, equivalent to $2{\cdot}6 \times 10^{-8}$ litre-torr per sec.

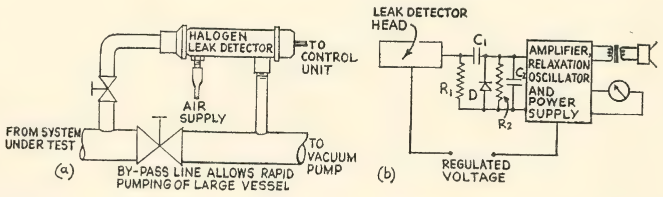


FIG. 9.20 National Research Corporation halogen leak detector (*after Torney*)

9.13. Comparison Between Various Leak Detection Methods

As will be ascertained by perusal of the foregoing sections of this chapter, the minimum detectable air leak by a given method will depend on several factors such as the volume of the system under test, the virtual leak present, the residual pressure, the effective pumping speed and variations of this speed at the detector, whether or not the system under test can be baked-out, the type of search gas used, the location of the detector in the vacuum plant and the nature of the device used to record the detector response. It is therefore difficult to make immediate comparisons between the various methods, but Table 9.3 is given to assist a correct choice. The figures given in this table are on the assumption that the plant is designed to give an optimum performance.

TABLE 9.3

Comparison between leak detection methods in which a search gas is used

Method	Pressure range in leak detector head, torr	Minimum detectable air leak, litre-torr per sec	Remarks
Single Pirani gauge	10^{-3} to 1		Backing space technique valuable, *see* § 9.7
with hydrogen		10^{-5}	
with butane		5×10^{-6}	
with CO_2		2×10^{-5}	
Single ionization gauge	10^{-8} to 10^{-3}		Similar results for hot- and cold-cathode gauges. If Bayard–Alpert gauge used, low pressure limit may be 10^{-10} torr. *See* § 9.7
with hydrogen		5×10^{-6}	
with butane		10^{-7}	
with CO_2		10^{-6}	
Charcoal-Pirani	10^{-6} to 1	4×10^{-7}	*See* § 9.8
Palladium-barrier	10^{-7} to 10^{-3}	10^{-8}	*See* § 9.8
Differential Pirani	10^{-6} to 1		*See* § 9.9
with butane		5×10^{-7}	
with CO_2		10^{-6}	
Differential ionization gauge	10^{-8} to 10^{-3}		*See* § 9.9
with butane		5×10^{-10}	
with CO_2		3×10^{-9}	
Nier mass spectrometer (hot-cathode ion source)	10^{-8} to 5×10^{-4}		*See* § 9.10 To achieve lowest source pressures ($<10^{-6}$ torr) instrument must be baked out.
with helium		5×10^{-10}	
with argon		5×10^{-9}	
with hydrogen		5×10^{-9}	
using electron multiplier	10^{-10} to 10^{-6}	$1{\cdot}3 \times 10^{-12}$	By accumulation technique; 6×10^{-14} litre torr-sec
Diatron with helium	10^{-8} to 5×10^{-4}	8×10^{-9}	
Nier mass spectrometer with cold cathode ion source	10^{-4} to 10^{-2}	10^{-8}	
R.F. mass spectrometer	10^{-10} to 10^{-5}	10^{-10}	Bake out necessary at pressures $<10^{-6}$ torr
Omegatron	10^{-10} to 10^{-6}	4×10^{-11}	By accumulation technique: 2×10^{-14} litre-torr per sec
Hot platinum halogen detector	Optimum 7×10^{-2} to 2×10^{-1} but can be used over wide range	3×10^{-8}	*See* § 9.12

9.14. Leak Detection in Ultra-high Vacuum Systems

In the attainment of ultra-high vacua, a mass spectrometer with electron multiplier recorder or an omegatron may be used to record leak rates down to about 5×10^{-14} or even 10^{-14} litre-torr per sec provided the instrument can be thoroughly degassed by baking and the leaked-in helium search gas is allowed to accumulate in the ion source for as long as one hour. Alpert (A9) points out, however, that very small leaks undetectable at higher pressures can yet be recorded comparatively readily at pressures of 5×10^{-9} torr or less if a Bayard–Alpert gauge is attached to the system. If for example, such a pressure prevails, on application of acetone, ether or carbon tetrachloride to the leak (usually a glass-metal seal or an ultra-high vacuum valve is the suspect location), either a rapid pressure increase to about 10^{-8} torr is registered or the organic liquid may temporarily close the leak and cause the pressure to decrease to 10^{-9} torr or less in a small system due to the electrical pumping action of the gauge. Alternatively, an isolation test is applied: the thoroughly degassed system (including the ionization gauge) is isolated from the diffusion pump by closing the ultra-high vacuum valve, and the subsequent rate of pressure rise is recorded by either operating the gauge intermittently or with a low ionizing current (*e.g.* 5 μA). These methods of operating the gauge prevent the rate of pressure rise from being reduced by the electrical pumping action of the gauge. Alpert reports a typical rate of rise during an isolation test on a satisfactorily vacuum-tight and degassed ultra-high vacuum system with a volume of 400 cc of only 3×10^{-11} torr per min, corresponding to 10^{-3} torr per 100 years. Rates significantly higher than this denote the presence of a leak; in practice, it is very important to be sure that a real leak is present and that excessive rates of pressure rise are not due to either virtual leakage because the system has not been adequately degassed or due to too high a conductance of the isolation valve when closed.

9.15. Standard Leaks

To calibrate leak-detection devices a standard leak which admits a certain gas at a known rate in litre-torr per sec is necessary. For leak rates above about 10^{-9} litre-torr per sec, the inlet pressure to the leak is usually at atmospheric pressure; for smaller leaks (*e.g.* for mass spectrometer leak detector calibration) it is usual to employ an inlet pressure of about 10^{-3} torr. It is practically very difficult to provide a standard leak with a throughput less than about 10^{-12} litre torr per sec.

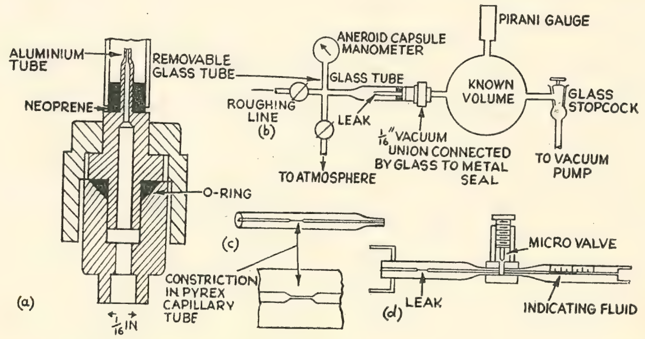


FIG. 9.21 Standard leaks and their calibration

For leak rates of about 10^{-5} to 10^{-8} litre-torr per sec, Ochert and Steckelmacher (OS2) recommend the use of a narrow bore aluminium tube which is squeezed flat at one end and joined to the vacuum system by the device shown in Fig. 9.21(*a*). A method of calibrating this leak (Fig. 9.21(*b*)) is to measure the rate of rise of pressure in a reservoir of known volume due to air admitted through the standard either from the atmosphere or from a roughly evacuated volume. Standard leaks required re-calibration at intervals, as their throughput may change due to blockage; air admitted should be filtered (*e.g.* by glass wool) to reduce the possibility of blockage by dust particles. Roberts (R19) has designed a standard leak (Fig. 9.21(*c*)) for leak rates down to about 10^{-8} litre-torr per sec which is made from Pyrex glass capillary tubing with a bore diameter of about 0·003 in. Near the centre of this tube is a constriction which is so small as to be only visible under a high-power microscope. To calibrate this leak its inlet end was connected to a very fine graduated glass capillary containing a short thread of indicating fluid (Fig. 9.21(*d*)). Other types of standard leak used include a plug of porous metal (§ 5.17) and porous ceramic. The Alpert ultra-high vacuum valve could also be used with advantage as a variable standard leak.

10

VACUUM COATING: THE DEPOSITION OF METALS AND OF NON-METALLIC SOLIDS

10.1. Introduction

A vast and specialized literature exists concerning the methods of coating solid objects (*i.e.* a substrate), and even the surfaces of liquids of low vapour pressure, with films of metals and of non-metallic materials of a suitably refractory character (Holland, H1; Auwärter, A13; Davy, D11; Heavens, H19; Mayer, M14; Strong, S8; United States Department of Commerce, US1; Yarwood, Y1). It is considered that the vacuum deposition of metals is well on the way to displacing most other techniques, such as electroplating, as far as the production of films of the order of 10^{-5} to 10^{-3} mm in thickness is concerned. The practical maximum thickness of evaporated films is 10^{-3} mm; thicker deposits may be obtained but are exceedingly brittle and tend to flake off. In such well-established industrial techniques as those of making mirrors for domestic purposes and the production of automobile headlamp reflectors, horn-button decorations, and even hub-caps and name-plates, vacuum coating methods have been adopted and may well be so to an increasing extent. Holland (H1) reports, however, that vacuum deposited coatings on metals with an adhesion comparable with that of electroplated deposits demand elaborate preliminary processing of the base metal to ensure freedom from surface contamination (*see, however*, § 10.6).

The vacuum deposition of metals has been applied to the making of mirrors for optical and domestic purposes, the aluminizing of cathode-ray tube screens, the production of special types of electrical resistors and capacitors, the manufacture of anti-static coatings on insulators, the fabrication of wind-screens which can be electrically heated for defogging and de-icing, the coating of artificial jewellery and of plastic articles for ornament and display, the preparation of matrices for the duplication of gramophone records, and to more specialized scientific appliances like the manufacture of photoelectric surfaces for photocells and iconoscopes. Furthermore, the vacuum deposition of thin films of certain dielectric materials has led to the availability in the optical industry of anti-reflection coatings, enhanced reflection coatings and interference filters, and may also be used for small special types of electrical capacitors.

The two chief methods of vacuum coating are:

(1) **The evaporation technique** in which the material to be deposited (*i.e.* the evaporant) is heated in a filament or crucible in an evacuated chamber so

that its vapour pressure increases to 10^{-2} torr or more; the ejected atoms or molecules then deposit on a substrate placed within the chamber at some distance from the evaporator. The maximum tolerable total gas pressure (excluding the vapour pressure of the heated evaporant) is 5×10^{-4} torr and pressures less than 10^{-4} torr are to be preferred.

(2) **The cathode sputtering technique** in which a cold discharge is set up by the application of a p.d. across two electrodes in gas at a pressure of 10^{-2} to 10^{-1} torr. One of these electrodes is a cathode of the metal to be deposited, the other is an anode. The substrate is placed to receive metal atoms from the cathode which are ejected by the incident positive ions in the gaseous discharge.

In general, the evaporation method is quicker, more adaptable, gives higher quality films and is much more suitable for the coating of intricate shapes with a uniform film. Sputtering is especially useful for obtaining deposits of the noble metals gold, platinum and palladium; whereas interest in sputtering tended to die out a few years ago because of the advantages of the evaporation method, revived attention has been devoted in recent years to the technique of **reactive sputtering** for the production of films of, in particular, the metal oxides.

In both cases the deposit forms atom by atom or molecule by molecule, *i.e.* there is no clustering of the deposit on the substrate surface unless the heating of the evaporant is unsatisfactory so that 'spitting' occurs. The atoms or molecules in the freshly formed film exhibit considerable mobility on the substrate surface. This mobility, which is particularly prevalent in films formed by evaporation, persists for some time after the deposition has ceased. This is similar to the case of films prepared by chemical deposition (Liepus, L16).

The overall quality of a deposit depends on the cleanliness—including freedom from adherent dust particles—of the substrate surface. It is not at all easy to fulfil this requirement, particularly in the case of large surface areas. Dust particles of the order of size of microns will produce pin-holes which, however, are not necessarily deleterious to the product (Tolansky, T5, T6), except in cases where protection against water vapour is required.

10.2. The Important Variables in the Evaporation Method

(*a*) *The temperature of the evaporant at the heated source* (§ 10.4).

(*b*) *The rate of evaporation of the evaporant at different temperatures* (Dushman, D1; Holland, H1; Rossmann and Yarwood, RY1).

(*c*) *The temperature of the target* (*i.e.* substrate on which the film is to be deposited). This should be low compared with the source temperature. Usually it is at or near room temperature but it may become undesirably overheated if it is too close to a source which undergoes prolonged heating. Water-cooled and even refrigerated targets are used in special applications.

(*d*) *The distance from the source to the target.* This is usually between 10 cm and 50 cm. Too short a distance will cause the source to overheat the target; too long a distance will give a uniform film but involve wastage of evaporant and long deposition times. Moreover, a large source-target separation may cause soft films to be formed with poor adherence unless the residual gas pressure is sufficiently low to ensure that the mean free path of the evaporant atoms in the residual gas is greater than (and preferably 10 times) the distance involved.

In continuous coating procedures, *e.g.* in the manufacture of capacitors, the distance might be only 2 cm, when zinc is used as the coating metal. The source must then be heat-shielded from the target and the target must move with a speed of the order of 25 ft per sec. If aluminium is used, a shield with a slit is arranged on top of the source and the target runs past the slit at a distance of 30 cm and at a speed of 2·5 ft per sec.

(*e*) *The angle of incidence of the atoms* (*or molecules*) *of the material at the target*. Perpendicular incidence is favoured to obtain maximum reflection of metal films and best adhesion of the deposit. It is often desirable to introduce a rotary movement of the target or the source—the former being simpler usually—to ensure perpendicular incidence and a uniform deposit on a large surface, or a re-entrant surface. A rotatable diaphragm between the source and the target can be used to control the thickness of the deposited film. Strong (S8) discusses the 'parabolizing' of an originally concave spherical mirror by the use of a diaphragm to produce a controlled variation of the thickness of an aluminium deposit on glass.

The necessary movement can be introduced mechanically from outside the vacuum chamber via Wilson seals (§ 4.24), O-rings (§ 4.21) or by electromagnetic induction. If electric motors are used *inside* the vacuum tank, their windings must be insulated by silicone varnishes (Allbright and Wilson) and, instead of the standard 'empire cloth', silicone-filled glass fibre cloth (*IOCO*) must be used for binding. Moreover, ebonite and bakelite insulators should *not* be used in the vacuum, but porcelain, steatite or polytetrafluoroethylene (*Fluon* or *Teflon*), the latter being preferable because of its flexibility. Fluon or Teflon washers (§ 4.26) are preferable to rubber washers because of their negligible gas evolution even at elevated temperatures.

(*f*) *The pressure and nature of the residual gas and the contaminating vapours produced by evolution during the cycle and by back-streaming from the vapour pump*. Before beginning the coating cycle, the pressure should be down to 10^{-4} torr, or, if high quality optical mirrors are to be produced, to 10^{-5} torr. There should be no appreciable evolution of gas when the metal is melted. This is often unavoidable so it is desirable to reduce its ill-effects on the deposit to be obtained by (*a*) using high speed pumps, (*b*) degassing the metal by heating it at a lower temperature than that eventually attained during deposition, (*c*) or, preferably, heating the metal to the evaporation temperature before inserting the target. This latter procedure would involve opening the tank to air during the cycle; to avoid this, a shield in the form of a metal flap can easily be rotated via a Wilson seal from outside the vacuum to be between the source and the target only during the degassing. Thus, in evaporating aluminium, beads of this metal are often formed on the tungsten spiral with the flap in place. To prevent evolution of gas from the walls, the

tank should be made of glass, or, since a metal tank is necessary for sizes above 18 in. dia and is often more convenient even in the smaller sizes, a choice should be made from the following: stainless steel or, for economy, stainless steel clad mild steel (Clyde Alloy, Ltd.); magnesium–aluminium alloy (I. A. Hughes); mild steel with a deposit of nickel–tin (backed by copper) (Tin Research Institute).

To reduce back-streaming, the methods discussed in § 2.10 should be adopted.

(*g*) *The state of the surface of the target due to its chemical composition and its pre-treatment influencing the appearance of the coating and its adhesion.*

It is appropriate to discuss here the preparation of a surface to be coated. One good method of cleaning the surfaces of optically polished glass parts, *e.g.* mirror blanks, is:

(1) use a cotton-wool or silk pad and rub the surface with lanolin,
(2) rub with powdered chalk,
(3) polish lightly with felt.

This procedure leaves a slight film of lanolin on the glass which is subsequently removed by ionic bombardment (§ 10.5). Some workers prefer wetting the glass surface with a 1 to 10% solution of the sodium salt of dioctylsulphosuccinic acid (Aerosol OT from the Cynamid Corporation, U.S.A., or Manucol OT from Hardman and Holden, Manchester, England) which is a specific wetting agent for silicates. The surfaces are then rinsed with distilled water of very good quality, having no smell, and then powdered with chalk and rubbed with silk.

Polished metal parts can be likewise cleaned before vacuum coating, but where the highest optical quality is not required, *e.g.* in the preparation of automobile headlamp reflectors, polishing is dispensed with nowadays and so is the use of an expensive base metal (§ 10.6).

In the evaporation of rhodium on to glass (§ 10.4) and also to ensure, as far as possible, freedom from pin-holes in mirror-making by the evaporation process in general, the following treatment of the glass before deposition is recommended:

(1) Wash the glass with soap (or a detergent, *e.g.* 'Teepol') and water.
(2) Rinse with freshly distilled water.
(3) Leave the glass in a 10% potassium bichromate solution for four hours.
(4) Rinse with distilled water again.*
(5) Wash with purified alcohol.
(6) Polish with a silk cloth.

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* Dr. F. C. Weil (*private communication*) recommends that, after rinsing, the glass plate should be withdrawn very slowly from the water (10 mm/min) and simultaneously heated by radiation so that it is perfectly dry as it leaves the water meniscus. The heating creates a violent 'steam blast' and avoids dust particles falling on the surface. The glass plate is then put in a metal gauze box until inserted in the vacuum chamber. This avoids the final polishing with a silk cloth (item 6). A final dry polishing will leave the glass plate electrically charged and able to retain firmly dust particles which are undesirable.

The potassium bichromate treatment has proved to be necessary because, without it, microscopic traces of rouge are left on the glass after it has left the optical polisher. If, then, the mirror is wiped after the metal is deposited, pin-holes remain.

Holland (H1) reports that glass surfaces which are badly contaminated with grease can be readily cleaned by immersion in water containing a detergent, and recommends a final cleaning with cotton-wool dipped in isopropyl alcohol.

A uniform film of water will cling over the whole surface of a chemically clean glass plate. A dried, clean glass surface will show a uniform breath pattern.

(*h*) *The time during which the surface of the target is exposed to the vapours.* This may vary from a fraction of a second (in continuous coating, where the space between the moving material and the surface of the boiling metal is filled with metal vapour) to minutes, when substances having low vapour pressures are to be deposited.

(*i*) *The measures adopted for improving the hardness of the deposit and its resistance to wear.* (*See* Weil (W10) regarding adhesion.) The intention here is to produce (by evaporation or otherwise) a transparent, firmly adhering and non-porous film of great wear resistance on the surface of the deposited metal (or other) film. The problem is a technically and fundamentally complicated one because the physical properties of thin films on a substrate are by no means the same as those of the bulk materials from which they are evaporated. Thus, magnesium fluoride is a softer material than silica, yet it is almost as good a protection against wear in the form of a thin film on a metallized surface. On the other hand, it is making a severe demand on protective films produced by evaporation that they be non-porous, and one cannot predict which materials will form pore-free films on the metal (or other) film to be coated, and, moreover, the underlying film will have an influence on adhesion.

Apart from being non-porous, the deposit must be amorphous as far as transmission of light is concerned, *i.e.* it must not deposit in micro-crystals of such size that a scattering of light takes place (*e.g.* as magnesium fluoride tends to do).

One method which has proved to provide a good surface protection for deposited metals and which fulfils the conditions stated above is to evaporate silicon monoxide, SiO, *in vacuo* on to the mirror. The monoxide is subsequently oxidized to silica, SiO_2 (§ 10.7).

10.3. Evaporator Elements or Boilers

Many patterns of filaments of helical, conical and straight forms using tungsten and other wires, and boats of molybdenum, crucibles, etc., have been described in the literature. Evaporators are commercially available from Bergen Wire Rope Company, Edwards High Vacuum Ltd., Heraeus GMBH, Kulite Tungsten Company, and Sylvania Electric Products Ltd.

Filaments heaters are usually made from non-recrystallized tungsten wire of about 99% purity (melting point 3380 ± 30° C) (Tungsten Manufacturing Company; Murex Ltd., G.E.C. Lamp Works) of which the ductibility is high at room temperature and reaches a maximum value at 100° C. On heating to 1000° C or more, tungsten re-crystallizes and becomes very brittle. To clean tungsten of its surface oxide, it can be rubbed with fine emery cloth or made the anode in a beaker containing a weak solution of sodium hydroxide with some other electrode as the cathode.

Tantalum (melting point 3000 ± 20° C) (Murex Ltd.), about twice the cost of tungsten, and molybdenum (melting point 2620 ± 10° C) (Johnson and Matthey; Murex Ltd.; Vactite Ltd.) are alternatives to tungsten; they are more readily worked but become very brittle on degassing by heating in vacuum.

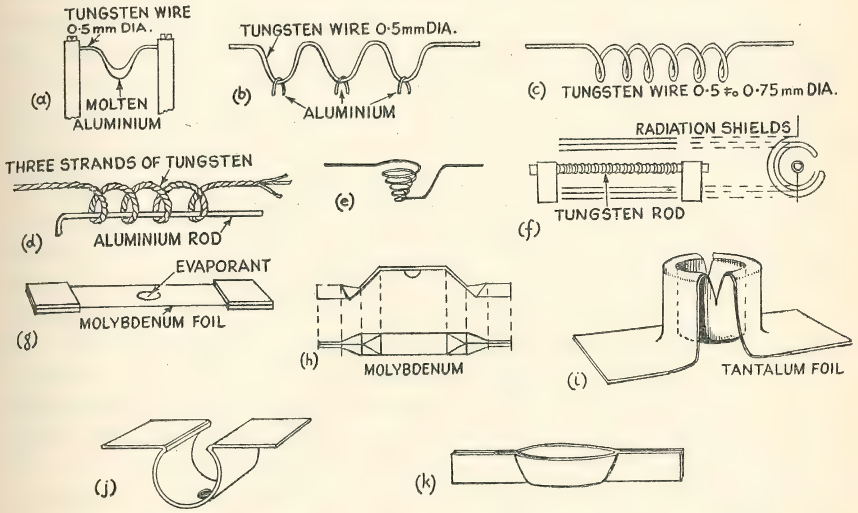

FIG. 10.1 Filament heaters and evaporator boats and crucibles for evaporation in vacuum

Boats and crucibles are generally made from molybdenum, tantalum or tungsten foil; the first of these is most frequently used.

Fig. 10.1 shows various types of filament heaters and evaporator boats and crucibles. The hairpin, sinusoidal, helical and multistrand filaments (Fig. 10.1(*a*), (*b*), (*c*) and (*d*) respectively) are only suitable for evaporant metals available in wire and thin ribbon form and which, when molten, wet the filament metal (§ 10.4). A filament wound in the form of a conical basket (Fig. 10.1(*e*)) is used for evaporating metals which are only available in pellet or granular form or which do not wet the filament (§ 10.4). In these cases, however, a metal foil boat is preferable. Type (*a*) serves as an approximate point source evaporator; it is loaded with a U-shaped loop of evaporant metal; types (*b*) and (*c*) are often used and similarly loaded with metals loops, but type (*d*) is particularly recommended for repeated use (ten or more times with re-loading when necessary) in batch operations; it is made from three (or more) tungsten wires twisted together before making the helix and then loaded with two or three straight pieces of evaporant metal wire. Not only does it hold considerably more metal, there is the considerable advantage that the molten evaporant flows over it to provide a uniformly coated source. In all these cases, if, as in the case of aluminium, limited solubility of the evaporant metal in the filament metal takes place, then the filament wire must be at least 0·5 mm in diameter.

Radiation shields around the source conserve heat, reduce power consumption and, moreover, can often be arranged to protect the target surface from radiant heat. The pattern due to Biram (B29) (Fig. 10.1(*f*)) is representative of good practice. It consists of a short thick tungsten rod with thin foil, tape or wire of the evaporant metal wrapped tightly and evenly round it. To prevent the evaporant from flowing into globules on heating, a thin wire of tungsten is wound round the heater rod at 1 to 2 diameters spacing with the rod ends left clear for electrical connections, which must be designed to permit the heater to expand in use. Three or four concentric quasi-cylinders formed by folding appropriately molybdenum or tungsten sheet are mounted on molybdenum supports around the heater to serve as heat shields. The bore of the central cylinder of this shield is about ¼ in.

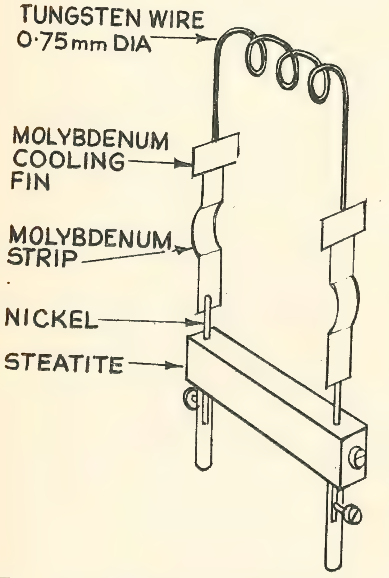

Fig. 10.2 Support for helical tungsten filament evaporator (nickel inserts used for molybdenum to tungsten and molybdenum to molybdenum welds)

It is common practice to support these filaments between steel clamps (the use of brass is deprecated because of the ready volatility of the constituent zinc) attached to the lead-in electrodes (§ 4.20). A more elaborate support for a helical tungsten filament is shown in Fig. 10.2 arranged so that sagging of the filament on expansion with heating is prevented. Note the cooling fins on the electrodes. Coating of the 0·75 mm dia tungsten wire with graphite is suggested to prevent alloying when aluminium is the evaporant, so permitting the filament to be used twelve times or more. The very small amount of colloidal graphite causes a thin skin of tungsten carbide to be formed which is not attacked by aluminium. As the metals tungsten, molybdenum and tantalum become brittle partly by recrystallization (especially those grades which do not contain the correct amount of 'inhibitors', Smithells, S17) and partly through attack by the evaporant (*e.g.* the frequently used aluminium) the problem of suspending large filaments to allow for expansion deserves more attention than it has received hitherto. With heavy gauge helical filaments, failure sometimes occurs on switching on a heavy current due to the magnetic field set up; this can also be avoided by arranging the supports to allow for expansion and also supporting the helix at its centre.

Alexander (A14) has patented a continuous evaporator in which the evaporant metal is fed continuously against a considerably over-heated tungsten rod so that it evaporates almost instantly. The arrangements for evaporating titanium in getter-ion pumps (§ 7.5) might well be considered in this context.

Evaporators in the form of boats and crucibles made from metal foil are also shown in Fig. 10.1. These are particularly suitable for metals which do not wet the heater and also for dielectric evaporants like magnesium fluoride and cryolite. Straight, flat foils of molybdenum, tungsten or tantalum may be used; Fig. 10.1(*g*) is a molybdenum foil with a central dimple to hold the evaporant; Fig. 10.1(*h*) is a more elaborate type (Edwards High Vacuum Ltd.) which resists warping at high temperature; Fig. 10.1(*i*) represents a cylindrical crucible of tantalum sheet (Heraeus GmbH) which is interesting in that the outer parts of the foil form a simple radiation shield; Fig. 10.1(*j*) shows a pattern favoured by Tolansky (T6); Fig. 10.1(*k*) shows a useful boat-shaped crucible.

These metal foil evaporators are clamped between steel jaws connected to the lead-in terminals and are heated by the direct passage of current from a step-down transformer capable of supplying 200 amp at 5 V r.m.s. for a molybdenum foil 20 mm wide, 50 mm long and 0·1 mm thick. Larger currents up to 400 and even 1000 amp may be necessary for larger boats of thicker foil; the lead-in electrodes must then be water-cooled.

The use of carbon is attractive as an evaporator element. Several metals can be readily evaporated from carbon crucibles, as was shown by O'Bryan (O3) who used electron bombardment heating (Fig. 10.3(*a*)). Rossmann and Yarwood (RY1) evaporated gold and silver from carbon crucibles of a novel design (Fig. 10.3(*b*)); these crucibles have a highly directional effect on the issuing evaporant, but different geometries could be readily devised.

Carbon would be a valuable material for evaporating large quantities of aluminium. Most literature references assert, however, that hot aluminium attacks carbon to form carbide leading to disintegration of the crucible. Our experiments indicate, on the contrary, that specially prepared carbons formed from very fine carbon black of average particle size less than 100 mμ and graphitized at above 2500° C during manufacture exhibit freedom from wetting and attack by molten aluminium in vacuum.

A suggested design of heater (Fig. 10.3(*c*)) for continuous coating, especially of aluminium, has not yet been used to any considerable extent, but it might well come into its own when the industrial applications of vacuum coating are extended. Thus, to ensure the economic coating with metals of wrapping paper, artificial leather and fabrics, speeds of travel of strips past the evaporator of at least 500 ft per min will be necessary, where the strip is about 3 ft wide. The problem of introducing the material continuously into a fore-vacuum lock and then into the high vacuum chamber (*see* B.P. 367,074 and 502,071) is by far not so difficult as the design of an evaporator which will work for hours without disturbance and evaporate several pounds weight of aluminium at a temperature of some 1500° C without being attacked.

The boiler consists of a slotted carbon heater tube ('Lamp' carbon is used, available from Morgan Crucible Co., Ltd., Powell Duffryn Ltd., General Electric Co., Ltd., and Siemens Bros.) and the boiler proper, which is electrically insulated from the heater. The latter should be made of the specially prepared carbon referred to above. Further details are given in the figure caption.

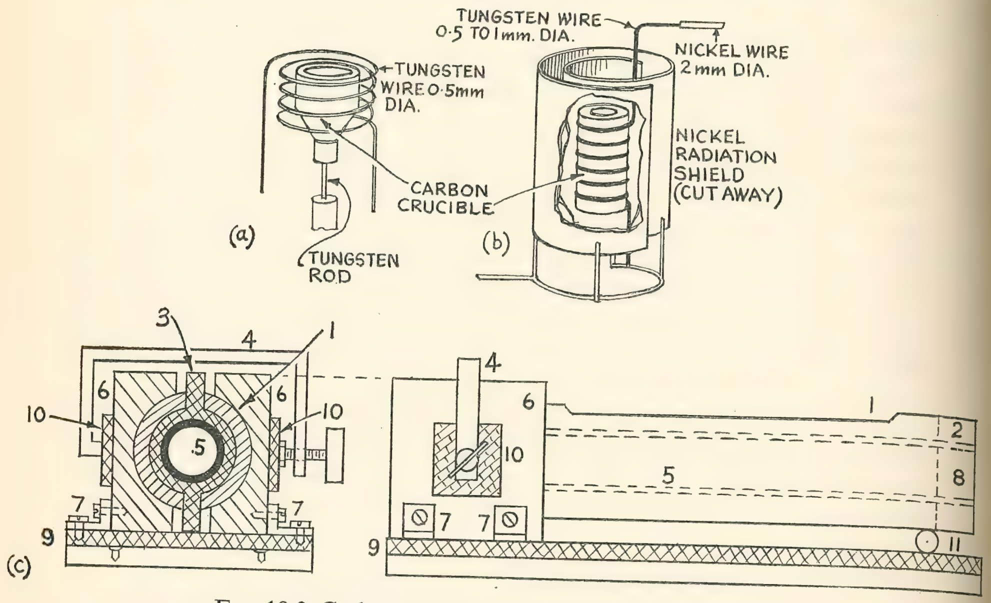

FIG. 10.3 Carbon crucibles for evaporation in vacuum

(*c*) A split heater tube 1 (of 'lamp' carbon) has a carbon ring 2 at one end and an insert of insulator 3 (aluminium oxide) at the other end. The boiler tube 5, provided with a slot opening for the evaporating metal, is made from the specially prepared carbon. One end of 5 rests in the ring 2 and the other end within 3. The ends of 5 are plugged with carbon discs, 8. Only one end of 5 is therefore insulated from the heater tube 1. The heater current is led to the heater tube by carbon blocks 6 via iron angles 7 which are bolted on insulation 9 (Syndanyo or Mycalex). The blocks 6 are clamped by 4 with insulation (aluminium oxide) at 10. The free end of the heater tube rests on the carbon roller 11. Current leads are flexible copper strips

Continuous coating with zinc is carried out on a commercial scale in the manufacture of capacitors, the paper dielectric being 1 ft wide, leading to improvements in weight, size and breakdown voltage as compared with laminated foil capacitors. An induction-heated bath in the form of a flat quartz crucible containing zinc is used as an evaporation source 12 in. long by $\frac{1}{2}$ in. wide which is at a distance of $\frac{1}{2}$ in. from the paper which runs at a speed of up to 1500 ft per min.

Other types of evaporator used are alumina or beryllium oxide crucibles with external heater spirals, radiation-heated sources in which the crucible containing the evaporant has a flat spiral tungsten heater above it, crucibles heated by electron bombardment (*e.g.* like that due to O'Bryan described previously, but metal crucibles can be used in place of carbon), and the type due to Milleron (M15) in which the tip of the evaporant wire (molybdenum and titanium were used) is fed through a cooled copper orifice directly into a beam of electrons which are accelerated to the wire by the application of a p.d. (*cf.* § 7.5). Finally, the possibility of using electromagnetic levitation sources (Okress, Wroughton, Comenetz, Brace and Kelly, OWCBK1) has been explored; the method here is to induce eddy-currents in the evaporant metal suspended in the magnetic field (*i.e.* without supports) between a pair of coils carrying alternating current at about 10 kc/s; estimates indicate that, with sufficient power, several pounds of aluminium may be 'levitated' and heated in this way, but difficulty is experienced because the aluminium drips downwards.

Table 10.1 gives approximate figures for a preliminary assessment of the electrical requirements for tungsten and carbon heater elements when they are used without radiation shields or heat insulation. The maximum temperature to be attained should be chosen as the basis for the calculation. The figures allow for conduction losses and surface roughnesses of the tungsten wires and sheets, and for the heat losses due to the conduction of carbon heaters.

TABLE 10.1

Temp., °C	Watt/cm² of surface		Resistivity in ohm-cm × 10⁻⁴		
	Tungsten	Carbon	Tungsten	Carbon	Graphite
1000	2·5	12	0·3	30 to 35	10 to 12
1250	6	24	0·45		
1500	13	45	0·49		
1700	22	65	0·55		
1900	37	110	0·62		

If the current I is in amp, the p.d. V in volts and the resistance R in ohms, l the length of the heater in cm, a the external surface area of the heater element in cm² (part at high temperature) and α the cross-section area of the heater, then the power consumption in watts is given by

$$W = IV = I^2R$$

and $R = \frac{\rho l}{\alpha}$, where ρ is given in Table 10.1.

W is determined by the temperature, the material and the external surface area a (*e.g.* it is 13 watt/cm² for tungsten at 1500° C Table 10.1), ρ is known at this temperature (*e.g.* 0·49 for tungsten at 1500° C) so R can be calculated. The necessary current I is then given by $I = \sqrt{W/R}$.

10.4. The Evaporation of Metals in Vacuum

A great variety of metals are evaporated in vacuum for various purposes. To assist in the choice of technique the most important metals concerned are listed together with notes. The figures given in brackets immediately after the name of the metal are, firstly, the melting point in °C and, secondly, the temperature in °C at which the vapour pressure of the metal is 10^{-2} torr. This second figure gives a rough but not too reliable guide as to the evaporation temperature; it is unreliable because in some cases, *e.g.* continuous coating of paper and plastics by zinc or aluminium, it may be desirable to exceed this figure considerably to achieve rapid, short-term evaporation. Moreover, in some cases, the heater may have to be at considerably greater temperature than the evaporant to achieve a satisfactory rate of volatilization, *e.g.* when chromium chips are simply placed in a conical heater.

Aluminium (660; 996). Begins to evaporate rapidly at 1100° C but best heated to 1200° to 1400° C. Wets heater freely. Use tungsten hairpin, helix or best three-wire twisted filament (Fig. 10.1(*d*)). Alloys with tungsten but not tungsten carbide, thus, a thin colloidal graphite coating on tungsten is an advantage. Molybdenum and tantalum boats can also be used. Some success has been achieved using carbon crucible of very fine, graphitized (2500° C) carbon black. To load the filament, small U-shaped pieces of aluminium wire or strip are pressed over turns; the stranded type filament, (Fig. 10.1(*d*)) boat, or crucible is simply filled with lengths of wire.

Aluminium films on glass, metals and plastics are widely used. The film has high overall white light and ultra-violet (down to 2000 Å) reflectivity. Holland (H1) shows importance of choosing 99·9% pure aluminium (Johnson and Matthey Ltd.) as compared with commercial 99% pure (impurities are chiefly Si and Fe, also Cu, Mn and Zn). For the highly pure material the reflectivity for normally incident white light is 92·5%; for the less pure metal it is about 3% less. At 2500 Å, the reflectivity is still 88%, rendering this metal especially valuable for optical mirror making as this figure is considerably greater than for silver, for example. The way in which the gettering of the residual gas by the evaporated aluminium affects the reflectivity of the film formed, is discussed by Holland (H20).

Aluminium films on glass are strongly adherent to the substrate and resist normal abrasion (*e.g.* due to cleaning with a Selvyt cloth) if they are deposited in a good vacuum (10^{-5} torr or less) and the glass is first cleaned (§ 10.1(*g*)) and subjected to ionic bombardment cleaning (§ 10.5). The resistance to abrasion is chiefly due to the formation of a surface film of oxide (Al_2O_3) which takes place on exposure to the atmosphere and grows in thickness over a period of several days. The film may be baked in air to accelerate the rate of growth of the oxide. Additional surface protection may be provided by anodizing, by a film of silica or magnesium fluoride (§ 10.7) or by lacquering (§ 10.6).

Antimony (630, 678). Use chromel or tantalum conical basket or molybdenum, tantalum or nickel boat. Chips or short lengths of the metal are placed in the evaporator; wets chromel. Evaporates very readily at the melting point. Film is highly reflective, somewhat greyish. A full account of antimony films, their properties and uses is given by Cremer and Ruedl in the book edited by Auwärter (A13).

Barium (717, 629). Evaporates readily from tungsten, tantalum, molybdenum, nickel or iron conical basket or boat. Wets without alloying. Chips of metal (which must be scraped clean) are placed in evaporator.

Beryllium (1284, 1246). Tantalum, tungsten or molybdenum conical basket or boat used; wets. Chips are placed in evaporator. Good reflector of white light and ultra-violet. Film protected by growth, in atmosphere, of transparent oxide film. Used for Lenard windows in X-ray tubes.

Bismuth (271, 698). Use chromel, tantalum, nickel or tungsten conical basket or boat. Chips are placed in evaporator. Evaporates readily to give film with reddish tint. Wets chromel.

Cadmium (321, 264). Use chromel, tantalum, molybdenum, tungsten, iron, or nickel filament, basket or boat. Either boat is filled with chips or filament is electroplated.* Sublimes readily at 264° C and above. Wets chromel. Does not condense readily on substrate unless very rapidly evaporated or, alternatively, a very thin film of, for example, silver is predeposited to form nuclei on which the cadmium condenses.

Calcium (810, 605). Tungsten conical basket or alumina crucible with external heater used; chips placed in evaporator.

Chromium (1900, 1205). Tungsten helix or conical basket used. Pre-fuse chromium on to tungsten in helium atmosphere or electroplate filament. Place chips in basket (inefficient). Produces extremely adherent, hard coating on glass which is an almost neutral 60% white light reflector. Sublimes. Aluminium film on chromium on glass provides excellent mirror with high reflectivity of aluminium combined with additional adherence of chromium. Transparent films have been used as optical density filters. Moore used solution for plating chromium on to tungsten consisting of 40 g of chromic acid, 0·4 ml of sulphuric acid in 160 ml of water. The plating current was about 1 amp per sq in. of anode area.

Cobalt (1478, 1649). Use tungsten filament or alumina crucible with external heater; electroplate filament. Alloys with tungsten. Olsen, Smith and Crittenden (OSC1) suggest that the cobalt should not have a mass greater than 35% of that of the tungsten filament to avoid fracture due to alloying.

Copper (1083, 1273). Use molybdenum, tantalum or tungsten filament, conical basket or boat. Place lengths of wire in basket or boat or electroplate filament. Does not wet heater readily. Reflective film with reddish tint.

Germanium (959, 1251). Tantalum, molybdenum or tungsten conical basket or boat used; wets tantalum and molybdenum. Reflective in visible region but transparent in infra-red at wavelengths greater than 10,000 Å. The electrical properties of thin germanium films have been studied by Dunoyer (D12).

Gold (1063, 1465). Tungsten or molybdenum helix, conical basket or boat used. Twist fine gold wire round thick tungsten filament or electroplate filament. Wets tungsten and molybdenum slightly. A reflective coating with distinctive reddish colour and selective green transmission. Used for shadow casting in electron miscroscopy and on metal oxide base layers to form conductive metal coating on glass (§ 10.11).

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* Electroplating methods for various metals are excellently described by Ollard and Smith (OS3).

Iron (1535, 1447). Tungsten helical coil used; electroplate on, or twist thin tungsten wire round, filament. Sublimes. Alloys with tungsten (*cf.* cobalt).

Lead (328, 718). Use iron, nickel, chromel or tungsten filament or conical basket or molybdenum boat. Twist thin lead wire round filament or place wire in boat or electroplate filament. Evaporates very rapidly; film has greyish appearance.

Magnesium (651, 443). Use tungsten, nickel, molybdenum or tantalum filament, conical basket or boat. Thin wire or ribbon is twisted round filament or placed in basket or boat. Or prefuse in helium atmosphere. Sublimes; no wetting. Highly reflective coating.

Nickel (1455, 1510). Tungsten filament or boat used. Electroplate (not more than 5% of mass of filament) or twist thin nickel wire round thick filament. If boat used, load with pressed mixture of tungsten plus 5% nickel. Coating tough and adherent with approx 60% white light reflectivity.

Platinum (1774, 2090). Fasten thin platinum wire or strip round tungsten filament with thin strands of tungsten, or electroplate tungsten. Reflects approx 60% of white light. Sintered on to Pyrex glass gives extremely tough coating. Alloys partly with tungsten. Best sputtered (§ 10.10).

Rhodium (1967, 2149). Tungsten filament electroplated with rhodium using Johnson Matthey solutions. Heraeus GmbH heat strips of rhodium directly to just below melting point. Films on glass reflects approx 80% normally incident white light; optically neutral. Extremely tough and adherent coating, used during World War II for mirrors in aircraft optical instruments. The use of rhodium mirrors has tended to decrease, probably due to the fact that improved pumps of high speed enable aluminium (which is much easier to handle) to be deposited in good vacuum conditions so that the film is adherent and tough. The optical neutrality through the visible spectrum of rhodium films renders them valuable for making optical density wedges. Zehden (Z1) has reported on the control of optical density in the manufacture of rhodium filters and stresses their advantages (neutrality, durability, slow evaporation rate leading to good control of thickness) and disadvantages (optical density increases slightly after deposition has ceased; burnishing of the film after deposition improves toughness but increases optical density).

To deposit satisfactory films of rhodium on glass, the residual gas pressure must not exceed 10^{-5} torr and be free of pump backstreaming vapours. Usually, therefore, a mercury diffusion pump with liquid-air trap is employed and it is best to clean the whole vessel by a glow discharge (§ 10.5) some time before the evaporation is begun. The vapour source is best prepared by winding about 15 cm of 0·5 mm dia tungsten wire on a 1 cm dia mandril and electroplating the helix in a rhodium bath.

Selenium (217, 234). Chromel, iron or molybdenum conical basket or boat or alumina crucible employed. Wets heater. Volatilizes very readily and tends to migrate all over interior of vacuum chamber. The disposition of effective shields in the plant, especially over the pump port, is important. In recent years, large evaporator plants have been constructed for the mass production of selenium rectifiers (*e.g.* Leybold's Nachfolger). Keck (K14), reported by Holland (H1), states that evaporated selenium films on chromium substrates are amorphous if the substrate temperature during deposition is less than 50° C and exhibit photoconductivity at wavelengths less than 5000 Å. For substrate temperatures of about 90° C, a hexagonal microcrystalline selenium deposit is formed with photoconductivity extending into the red region of the spectrum. If 5 to 9% by weight of tellurium is added to the selenium the photoconductivity is increased but the resistivity is decreased.

Silicon (1410, 1343). Only satisfactory method is to use a crucible of beryllium oxide with an external tungsten heater. Unless exceptional precautions (*i.e.* maintained pressure of less than 10^{-5} torr during deposition) are taken, the film will contain silicon monoxide. Films on glass are amorphous and highly durable.

Silver (961, 1047). Use tantalum, molybdenum or tungsten filament, conical basket or boat. Electroplate filament or place short lengths of silver wire in boat. A highly reflective film (94% overall white light reflectivity when fresh) but deteriorates on exposure to atmosphere. Transparent coatings show selective blue transmission. Films not strongly adherent to substrate. Used as transparent films in interferometry, *e.g.* for Fabry-Perot interferometer.

Tin (232, 1189). Use tungsten or molydenum filament, conical basket or boat. Electroplate filament or place in basket or boat. Wets molybdenum. Reflective coating, but tends to milky appearance as thickness increased beyond opaqueness (Holland, H1).

Titanium (1727, 1546). Tungsten or tantalum filament or conical basket; tungsten foil or boat. Hass (H21) recommends evaporation at pressure less than 10^{-5} torr from a directly heated tungsten strip at 2000° C, currents of the order of 200 amp being necessary. The film can be converted to titanium dioxide by heating in air at 400° to 450° C; the dioxide has rutile structure with high refractive index, valuable as enhanced reflection layers and in the manufacture of interference filters (§ 10.9). Excellent adhesion to glass. The evaporation of titanium in vacuum has also led to the development of the getter-ion pump (§ 7.4).

Uranium (1132, 1898). Use conical basket of tungsten or tungsten boat. The deposit oxidizes readily. Employed in shadow casting in electron microscopy.

Zinc (419, 343). Tungsten, molybdenum, tantalum or nickel filament or conical basket used; electroplate on filament or fill basket with chips. Sublimes very readily. Used deposited on paper in capacitor manufacture. Like cadmium does not condense readily on substrate unless very rapidly evaporated or nucleation centres (*e.g.* of silver) pre-deposited.

Carbon may be evaporated *in vacuo* by using pointed carbon rods pressed together; heavy current passed through the rods produces intense heating at the high resistance contact between the tips of the rods. Bradley (B30) used 0·5 cm dia carbon arc rods in 0·6 cm i.d. silica tubing holders mounted in bosses screwed to uprights with one carbon electrode fixed and the other spring-loaded (to press carbon tips together) by small spring of 0·01 in. dia tantalum or tungsten. A current of 20 to 50 amp was necessary. Carbon films are used in specimen preparation for electron microscopy.

The distribution of the evaporated metal in the vacuum system depending on the source configuration is considered in detail by Holland and Steckelmacher (HS3). The evaporation in vacuum of the radioactive metallic isotopes tungsten 185, chromium 51 and gold 198 to study the distribution of the evaporant has been undertaken by Preuss (P10) and by Preuss and Alt (PA1). Inman and Quigley (IQ1) give a design of a vacuum evaporator for radioactive and toxic (*e.g.* beryllium) metals and discuss the difficulties of decontaminating the chamber and the disposition of effective shields. Earlier, Heavens (H22) used radioactive tracer heater elements (tungsten and tantalum) to show that in evaporating silver and germanium, more contamination of the deposit by the heater metal was obtained than would be expected from relative rate of evaporation considerations. Chomet and Yarwood (CY1) evaporated silver containing the radioactive isotope, silver 110, to study the diffuse reflection of a beam of silver atoms at a hot target and showed that it was in accordance with the Knudsen cosine law.

10.5. Vacuum Coating Plant

Laboratory plants for the production of small numbers of coated articles have been described in several texts (Holland, H1; Strong, S8; Yarwood, Y1). A design of a readily constructed apparatus for experimental work which uses a 12 in. dia Pyrex glass bell-jar as the vacuum chamber is shown in Fig. 10.4, whilst Plate 6 illustrates a commercial plant with an 18 in. dia bell-jar. For laboratory experiments where fast operating cycles are not required, the 12 in. plant (Fig. 10.4) can be satisfactorily pumped by a 2 in. port dia oil diffusion pump with a water-cooled baffle providing a speed of about 70 litre per sec at 10^{-3} torr, and backed by a two-stage mechanical rotary pump (preferably with gas-ballast provision) of displacement about 50 litre per min. A larger 4 in. port dia diffusion pump (speed: 300 l/s approx) is, however, preferable, but expense is often a consideration in small-scale work. If fast pumping cycles and repeated operation are necessary, as in the production of optical mirrors, the necessity for high pumping speed cannot be over-stressed. Thus, the commercial gear shown in Plate 6 employs a 9 in. port dia oil diffusion pump (speed: 1500 l/s approx) to evacuate an 18 in. dia bell-jar of about 100 litres capacity. Holland (H1) recommends a pumping speed of 5 l/s for every litre capacity of the chamber for normal operation and 10 l/s for every litre in the metallizing of plastics (§ 10.6) in routine production. These high speeds are demanded not only to ensure a rapid operating cycle but also to remove as quickly as possible the gases liberated by the vapour sources, the articles to be coated and the walls of the vessel. When using the necessary large diameter diffusion pumps (the port diameter may be half the chamber diameter) it is of the greatest importance to prevent back-streaming oil from reaching the chamber in any significant amount. This demands an efficient water-cooled baffle between the chamber and the diffusion pump.

A Pirani gauge or a thermocouple gauge is most convenient for measuring the backing pressure, whilst the Penning gauge is probably the best choice for measuring the chamber pressure before deposition is commenced.

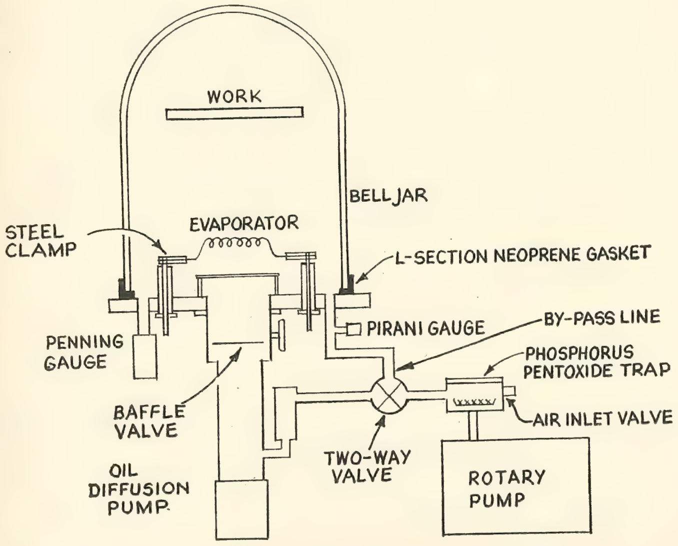


FIG. 10.4 Laboratory plant for vacuum coating by the evaporation process

As mentioned in § 10.2(*g*), it is the usual practice to subject the surfaces to be coated to the scavenging action of the high energy positive ions produced in a glow discharge before the evaporation is begun. This additional **ionic bombardment cleaning** has a marked effect in improving the adhesion of the evaporated film to the surface. Important points to be observed are:

(1) To prevent transition from a glow to an arc discharge, a high reactance transformer should be used or a series limiting resistor employed.

(2) The cleaning action of the positive ions which impinge on the substrate surface to be coated is most effective when this surface is in, or close to, the cathode dark space region. This requires a residual gas pressure of between 10^{-2} and 2×10^{-2} torr.

(3) The effectiveness of the cleaning action is primarily decided by the power consumed in the discharge. Provided that the p.d. across the electrodes exceeds 2 kV, the product of the voltage and the current is the significant quantity. Suitable figures for a 12 in. chamber are 3 kV at 100 mA and for an 18 in. chamber, 3 kV at 200 mA.

(4) The electrodes should be made of aluminium, which does not sputter significantly.

(5) An alternating or a steady voltage supply may be used, the former being

usual because rectifiers are avoided. Holland (H1) deprecates the practice of using a single insulated discharge electrode in the chamber and the earthed base-plate as the other electrode if an a.c. supply is employed. Though convenient, this practice leads to sputtering of the base-plate metal and of any metal fittings within the chamber at earth potential. Furthermore, the discharge is liable to spread into the diffusion pump, warm the baffle region, and so enhance the entry of pump fluid into the work chamber. The best practice is to use an H.T. transformer with both output terminals insulated from earth and connected to insulated aluminium electrodes. Fig. 10.5(*a*) shows an arrangement suitable for a small plant with a fixed glass plate on to which the metal is to be evaporated; Fig. 10.5(*b*) illustrates the use of sector electrodes for ionic bombardment of glass placed on a work holder which can be rotated to ensure uniformity of the deposited film thickness over a large surface area. An aluminium shield above the exhaust port is used to prevent the discharge from entering the pump. If, however, a rectified a.c. supply is employed, the positive terminal can be earthed and a single insulated aluminium electrode mounted within the work chamber. Condensers should be avoided in the rectifier circuit as they tend to cause change-over of the discharge to an arc.

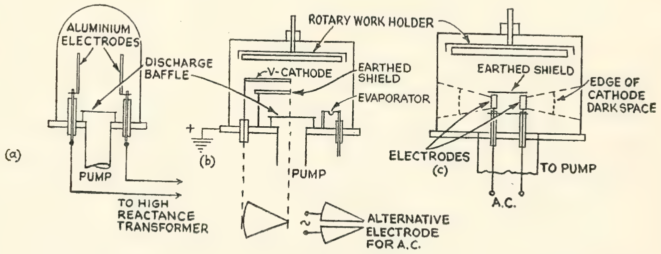


FIG. 10.5

(*a*) Arrangement of electrodes for ionic bombardment cleaning in a small plant
(*b*) The use of sector electrodes in a large plant with a rotary work holder
(*c*) Use of shielded electrodes (*after Holland*)

Recently, Holland (H23) has shown that if the vacuum coating plant is evacuated by an oil diffusion pump so that hydrocarbon vapours are present in the discharge, then electrons in the glow discharge may produce surface coatings on the glass to be coated; if silicone pump fluids are used, moreover, decomposition products which are readily wetted with water are formed on the glass. It is therefore recommended that the bombardment of the glass should be by random positive ions and that the cathode electrode should be shielded to prevent direct electron bombardment of the glass. A suggested arrangement of electrodes to ensure this is shown in Fig. 10.5(*c*). The two aluminium bar electrodes are arranged with a gap between them which is small enough not to sustain ionization therein at the pressure and current density used, so that the discharge follows the longer path shown in the diagram. These electrodes are covered with a shield. With an applied alternating potential of about 5 kV and at a pressure of 10^{-2} torr, the glass is randomly bombarded by energetic positive ions but energetic electrons cannot reach it.

(6) This discharge cleaning is often done at the backing pressure provided by the mechanical rotary pump used alone. This is not good practice for two reasons:

(*a*) at the order of pressure required for a satisfactory dark space region (10^{-2} to 2×10^{-2} torr) the rotary pump has low pumping speed so that the pressure will fluctuate;

(*b*) it is best to commence the deposition of the film as soon as possible after the discharge cleaning is ended.

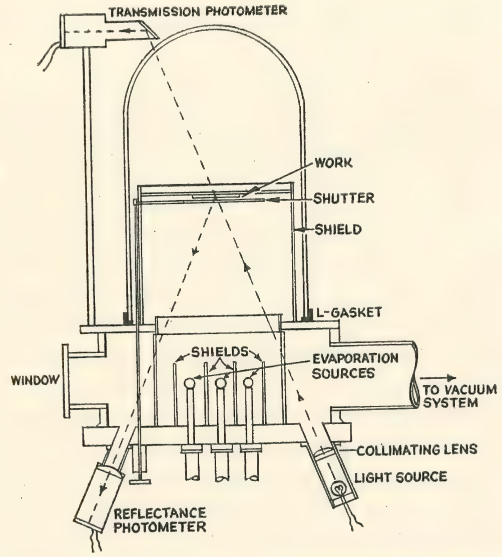


FIG. 10.6 Vacuum deposition plant for obtaining films of controlled light transmission (*after Hass*)

Preferable practice is therefore to have both the diffusion and the rotary pump working and admit air through a needle valve to provide the necessary pressure for sustaining the glow discharge.

Alternatives to ionic bombardment cleaning are electron bombardment (Rice, R20 and Dimmick, D13), which has not been used extensively, and radiant heating. In the manufacture of durable, magnesium fluoride anti-reflection films (§ 10.9), the surfaces to be coated are heated to 250° to 300° C after the ionic bombardment cleaning. An arrangement of electrically heated Nichrome wire spirals fitted into a spherical reflector shield is disposed within the work chamber to heat by radiation the optical components concerned (Fig. 10.11).

To deposit by evaporation a film of known light transmission the plant designed by Hass (Fig. 10.6) is recommended. The 'base-plate' is an annular well so that fittings can be made into its side wall. The collimator lens is sealed by O-rings and a narrow light beam is provided to prevent stray reflections from occurring. It is good practice to modulate the light beam by a rotating sector and then use an a.c. amplifier attached to the photocell monitor, as any stray steady illumination of the photocathode is then not recorded. Optical filters may be placed in the beam as required. Alternative ways of providing metal films of controlled thickness are (*a*) to use a known mass of the evaporant and (*b*) to include near the substrate a small glass plate with vacuum-deposited end electrodes; the electrical resistance of the film formed on the plate between these electrodes is then monitored during the deposition. If either of methods (*a*) or (*b*) is used, a number of preliminary calibration runs is necessary.

10.6. The Evaporation of Metals on to Plastics, Lacquered Substrates and Paper

The procedure adopted is similar to that for coating glass. However, difficulty with considerable outgassing and/or desorption of moisture from the substrate is experienced, and it is undesirable to expose the substrate to radiant heat from the evaporator source. High pumping speed must therefore be maintained, and the evaporant metal (usually aluminium) must be volatilized quickly in a few seconds to prevent undue temperature rise of the substrate surface. Though small plastic articles may be coated in conventional plant provided that a self-purifying diffusion pump is used if plasticizer evolution takes place, the vacuum plant for the production of several coated plastic articles in a single batch or the continuous coating with metal of a roll (which is unwound within the vacuum chamber) of plastic or paper comprises a diffusion pump backed by an ejector pump and a rotary pump. The ejector or booster pump (§ 2.18) has a high speed at the intermediate pressures of about 10^{-1} torr at which both the diffusion pump and the rotary pump speeds fall off considerably; moreover, the ejector will operate at a high backing pressure of up to 3 torr so that a comparatively small rotary backing pump will serve. This ejector pump may form part of the backing stage of the diffusion pump itself in a booster-diffusion combination. A suitable plant layout including a holding pump is shown in Fig. 10.7; Fig. 10.8(*a*) indicates the arrangement of the rotatable work holder for the coating of a number of small plastic components; Fig. 10.8(*b*) shows a set-up used for depositing aluminium on lacquered automobile headlamp reflectors; Fig. 10.8(*c*) indicates how a roll of paper or plastic is unwound in the vacuum chamber as it is coated with metal.

Polymethyl-methacrylate (Perspex, *see* § 6.6) and polystyrene are transparent plastics which are used in the optical industry for lenses and mirrors in place of glass. These can be directly coated with aluminium in vacuum but the adhesion of the film is poor and the surface is soft, particularly on the methacrylate. Ionic bombardment cleaning may be used with discretion; it is essential to limit the intensity and time of the discharge cleaning otherwise discoloration of the plastic occurs. Electrically conducting vacuum deposited metal films on acrylic mouldings are also used and there is some possibility that 'printed circuits' of copper on plastic substrates may be prepared by developments of the vacuum deposition technique.

The considerable developments that have taken place in the vacuum metallizing of plastics have, however, resulted from the technique of first coating the article with a tough adherent lacquer. The sequence of operations (Bateson, B31) is then annealing and pre-cleaning of the plastic, dipping in lacquer for undercoating, baking, aluminizing in vacuum, dipping in lacquer for top coating, dip-dyeing (if required) and baking.

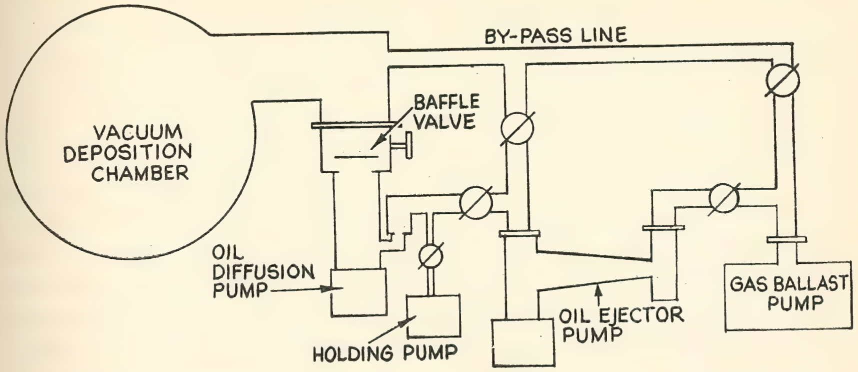


FIG. 10.7 System for aluminizing volatile substrates such as plastics, lacquered surfaces or paper

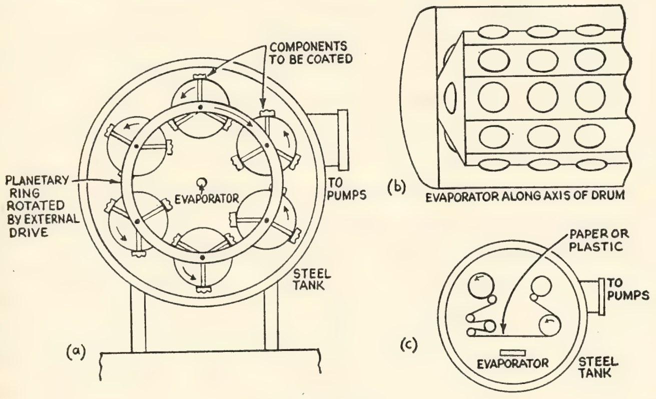


FIG. 10.8

(*a*) Rotatable work holder for the metallizing in vacuum of a number of small components

(*b*) Arrangement in vacuum chamber of lacquered reflectors to be aluminized

(*c*) Vacuum coating of roll of plastic or paper

The method of first lacquering the substrate before the vacuum deposition of the metal has also been applied to the coating with aluminium of metal substrates, and, in particular, to the mass production of headlamp reflectors for bicycles and motor-cars. As it is uneconomical to polish the metal itself and, moreover, a high degree of optical finish is unnecessary, an inexpensive mild steel blank is pressed out to the correct surface contour, buffed for a few seconds—no specular reflection—and is then dipped into a viscous organic lacquer (viscosity of 1 to 5 poise, glycerol being 1). A solution, or a plastic without a solvent at a temperature at which it is liquid, can be used: for example, plastics of one of the polystyrene, vinyl, phenol-formaldehyde or melamine-formaldehyde groups. The metal blank is withdrawn slowly from the lacquer—special machinery has been designed for dipping—and droplets are carefully removed by wiping. The result should be a glossy surface, free from 'waves'. After drying and stoving to the correct temperature—which is commonly done by infra-red radiation in a tunnel well-ventilated with filtered air—the metal coating, preferably aluminium, is deposited in vacuum (Fig. 10.8(*b*)). The aluminium film may then be protected by a top lacquer coating, but the more usual practice is to seal it within the headlamp housing, where it is protected against abrasion and dust. Developments of this kind might well lead to methods of protecting thin steel plate against rust.

Firms which supply suitable lacquers are W. Canning and Co., Ltd., Creators Ltd., Croid Ltd., Dow Chemical Ltd., I.C.I. Paints Division, Phenogeaze Ltd., Thornley and Knight Ltd.

Cheap jewellery and fancy goods made from artificial resins by pressing in a mould (acetyl cellulose should be avoided, if possible, because it is strongly hygroscopic) have also to be lacquered in order to acquire good lustre after vacuum coating. The lacquer must be chosen so that its solvent does not attack the plastic of the article. It must also adhere well and must not 'craze' on drying (some lacquers containing linseed oil tend to do so when dried too quickly). Furthermore, the deposited metal must adhere well to the dried lacquer, which must not release gas during the deposition.

A usual need is to produce lustres of different colours. As it is difficult to obtain repeatable results by depositing two metals of different colours simultaneously, top lacquers, *i.e.* superimposed on the metal coating, are used. Generally, transparent lacquers which can be tinted by dye solutions are employed (Vevers and Gardam, VG1; Bateson, B31; Holland, H1). If a solution of a polymerizing plastic or the solvent free plastic is used as a lacquer, *e.g.* an epoxyethane resin like Araldite (§ 4.14) or Epikote (Shell Chemicals Ltd.) or a polymerizing styrene lacquer (Catalin Ltd.), then, after drying to an absence of tackiness, stoving can be to a temperature at which total polymerization would take place if continued long enough (*e.g.* 1 hour). However, heating is interrupted before such polymerization is complete (*e.g.* after 50 min). Such temperatures are 180° C for Araldite and 75° C for the styrene lacquer. The metal is then deposited in the vacuum chamber (Fig. 10.8(*a*)) and the additional stoving necessary to complete the polymerization is carried out subsequently. This results in a very strong adhesion of the metal coating, probably due to the fact that the slightly coalescing molecules of plastic on the surface 'grip' the metal atoms which are embedded in them and 'anchor' them (*see Brit. Pat.* 710,643 (1954)). If the preliminary polymerization has not been carried far enough, the deposit will show ripples, doubtless due to the fact that the aluminium coating is rigid and incompressible compared with the deformable polymerized lacquer.

Further recommendations as to suitable lacquers for plastics and metals and their suppliers are made by Edwards High Vacuum Ltd. in their information sheet H.106/2. For lacquering cellulose acetate or cellulose acetate butyrate, 'Evapoplast' (Nu-Finishes Ltd.) may be used as a base lacquer and as a top lacquer, *i.e.* on the plastic and on the vacuum deposited metal film respectively. The lacquer is applied by dipping or spraying with 8 parts of lacquer to 1 part of 1342 catalyst, the latter being required to decrease the stoving temperature; stoving at 55° C for 4½ hours is recommended. For lacquering polystyrene, the base lacquer 'Edosol A' is suggested with 'Edosol B' as the top lacquer. These must be sprayed on and stoving is at 50° C for 2 hours. The suppliers are Ferguson Edwards. Alternatively, lacquer X2176 (W. Canning and Co., Ltd.) may be used for both base and top coats, stoving being at 50° C for 1 hour. This last firm also supplies 'Lactrene' and 'Erealene' which are suitable base lacquers for spraying on to the surfaces of three dimensional mouldings of methacrylates like Perspex or Lucite before they are vacuum-coated with metal. If urea or phenol formaldehyde is to be vacuum-coated with metal, 'Evapoplast' can be used *without* the catalyst for both the base and top lacquer.

To lacquer metal surfaces to be vacuum-coated for decorative articles, 'Synolac' E91X is recommended for the base lacquer and 'Synolac' top lacquer film for the top coat. These are applied by dipping or spraying and dried for 10 min before stoving at 120° C for 1 hour. The suppliers are Cray Valley Products. Alternatively, 'Vitros' 345 (Griffiths Bros.) may be used for both base and top lacquer. For metal reflectors (*e.g.* for automobile headlamps) an acrylic type lacquer is recommended which is applied by dipping, allowed to dry in air for 10 min and then stoved at 120° C for 1 hour. Suppliers are Carrs Paints Ltd.

To dye the top lacquer to various colours, 'Frigilene', available in a variety of hues, may be used. This is dissolved in spirit and the top lacquer film dipped into it. This material is supplied by W. Canning Ltd.; Geigy Ltd. also supply suitable spirit dyes.

A further method of increasing the 'grip' of a metal film on a surface is to pre-deposit 'nuclei' of another metal capable of increasing the adhesion energy of the final deposit. Thus, a slight film of silver pre-deposited in vacuum on paper in the production of capacitors improves greatly the adhesion of the subsequently deposited main film of zinc. The problems of degassing and depositing zinc or aluminium on paper and on plastic sheet are discussed by Holland (H1), Holland and Hacking (HH1) and Clough (C5).

10.7. The Preparation of Protective Surface Layers on Glass and Deposited Metal Films

A useful and effective method of providing a hard protective film on a glass or metal surface is to evaporate silicon monoxide, SiO, with subsequent oxidation to silica, SiO_2 (Hass and Scott, HS4).

Finely divided silicon (high purity, iron-free) of about −200 to 300 BSS, *i.e.* having maximum size particles of about 0·07 mm dia, is thoroughly mixed with equally fine quartz, preferably made from clear Brazilian quartz crystals which are disintegrated first by quenching from about 500° C and second in an impact mill. The proportions of the mixture should be approximately in the ratio of the molecular weights, a small excess of quartz not being objectionable. A suitable intimate mixture known as Viacote 'Q' is supplied by Vacuum Industrial Applications Ltd. The mixture is placed in the closed end of a silica tube which is evacuated to 10^{-4} torr and heated in a horizontal muffle furnace to about 1150° C. The silicon monoxide evolves from the mixture and condenses on the cooler parts of the surface of the tube. The resulting powder can be evaporated in vacuum from a tungsten, tantalum or molybdenum boat—tantalum being preferred—in the shape of an ellipse 2½ in. by 1 in. formed from a piece of tantalum 4 in. × 1¼ in. × 0·008 in. This boat requires a heating current of 250 to 300 amp to reach the correct evaporation temperature. A deposited film of about 1500 Å (0·15 μ) in thickness forms in about 10 min on the surface of a glass target placed at 10 in. approx from the boat. The correct thickness is obtained when the interference colour, after having passed once through the range of spectral colours, becomes red a second time.

The silicon monoxide layer formed is then heated in air to 100° C for 50 hours in order to oxidize the SiO to SiO_2.

Apart from being valuable in protecting the surfaces of deposited metal films, such silica layers on glass optical components form a protection against weathering and, as such, are particularly useful under tropical conditions. In depositing the monoxide on to glass in vacuum, the glass is given the usual degassing and cleaning treatment by ionic bombardment (§ 10.5). Silicon monoxide is sensitive to contamination by hydrocarbons because the deposit always contains traces of free silicon.

If protected mirrors on plastics are required, it is advisable first to subject the plastic blank to cleaning by ionic bombardment, deposit a thin film of silicon monoxide to a thickness at which the first red in the interference colours is first shown, then deposit the metal on this monoxide layer and, finally, the protective monoxide layer. Subsequent heating to form silica then follows as before.

In a continuous production schedule, it is not necessary—though it is preferable—to make the silicon monoxide first and then evaporate it. The mixture of ground quartz and silicon can be used instead, provided that it is really intimately mixed by wet grinding. It should not be stored, however, because it has been found that it deteriorates and gives erratic results after a few weeks for reasons not yet known.

A method of forming very hard protective surfaces on certain metals is by **anodizing.** For the protection of aluminium films on glass either the aluminium itself is anodized to aluminium oxide or silicon is deposited on the aluminium and the silicon anodized to silica.

A suitable electrolyte for anodizing consists of 3% tartaric acid in distilled water with ammonium hydroxide added to make the pH equal to 5·5. To anodize an aluminium film on glass (a good adherence of the film to the substrate is essential, thus some substrates, *e.g.* mica, will not serve) it is made the anode in the electrolyte with an adjacent parallel sheet or mesh of super pure (99·9%) aluminium as the cathode. A rectified, smoothed power supply of up to 200 V is used. For anodizing aluminized mirrors about 12 in. square, Holland (H1) recommends a supply of 150 V at 2 amp. As the oxide film is insulating, its maximum thickness is limited by its growth to a specific repeatable value dependent on the applied voltage and is complete within about 2 min. The oxide thickness does not increase linearly with anodizing voltage except above 40 V, but the mean rate of increase of film thickness may be taken to be about 13 Å/V. It is possible to anodize thin aluminium films until they consist entirely of aluminium oxide; for the surface protection of full aluminized mirrors, an oxide film thickness of at least 0·15 micron should be obtained.

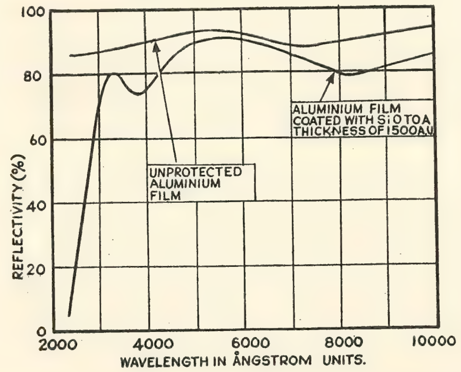


FIG. 10.9 Reflectivity of protected and unprotected aluminium mirror (*after Hass and Scott*)

For maximum reflectivity in visible region the optimum thickness of SiO is 1500 Å deposited in 10 min. To obtain this thickness in practice, evaporation of SiO should be stopped when the interference colour has passed through yellow, red and green and has become red again

To provide a protective film on aluminium, silicon monoxide is evaporated in vacuum from a tungsten boat on to the aluminium; it can then, if desired, be anodized to form silica. It is likely that there is an advantage in ageing the aluminium films in air for about 24 hours before depositing the silicon monoxide on them, so producing a layer of aluminium oxide. When the silicon monoxide is later anodized, the aluminium oxide combines with the silica to form a hard glaze. The graph of Fig. 10.9 shows the reflectivity of a protected and an unprotected aluminium surface in the wavelength range from 2500 to 10,000 Å when the silicon monoxide coating has a thickness of 1500 Å. In the visible region of the spectrum the protected aluminium is almost as good as the uncoated film; in the blue and ultra-violet there is an appreciable fall in reflectivity, but it is still in the region of 80% at 3660 Å (the wavelength of the mercury line used in some copying processes). In the infra-red, the reflectivity of the protected film is about 95%.

Titanium dioxide (§ 10.4) can also be produced by anodizing, and magnesium fluoride films (§ 10.9) can be used for the protection against weathering and abrasion of aluminium, but the best results are achieved by the use of silica.

The resistance to abrasion of protected and unprotected films on surfaces can be tested with a $\frac{3}{4}$ in. steel ball covered with rough linen, loaded with a 500 gram weight and subjected to a reciprocating motion. Anodized and silica-protected aluminium films are not affected by as many as 1000 cycles of such motion, whereas unprotected films are eroded. The corrosion resistance of the film is tested by boiling the mirror in 6% NaCl solution for at least one hour. The reflectivity of a silica-protected mirror remains unchanged after such treatment, showing that it is impermeable. It is also resistant to seawater, sodium hydroxide and many acids, but is removable by treatment with a solution of hydrochloric acid and copper sulphate.

10.8. Some Further Applications of Evaporated Metal Films

If a thin film of aluminium is deposited on the inner surface of the fluorescent screen of a cathode-ray tube the light output from the phosphor can be increased by as much as 80% for the same power input and accelerating voltage at the electron gun. This is because the electrons incident on the screen are able to penetrate the thin aluminium film which acts as a mirror to ensure that the light from the fluorescent image is almost all thrown forward towards the observer. This practice is now universal in the manufacture of television cathode-ray tubes. To provide a suitable aluminium film, the inside surface of the fluorescent screen is first coated (in air) by a thin fluid plastic film. This film covers over the rough surface presented by the phosphor particles of the screen so that the surface presented to the inside of the tube is smooth. A stream of warm air is then blown through the tube to drive off the plastic solvent. The tube is then evacuated to 10^{-4} torr or less and aluminium evaporated on to the screen. After the aluminium has been deposited the tube is baked to drive off the plastic film and leave aluminium adhering to a small fraction of the phosphor particles. The film thickness is about 500 to 800 Å.

The usual arrangement of the vacuum plant in mass production is to provide a trolley with a fractionating oil diffusion pump and a mechanical rotary backing pump for each cathode-ray tube. Suitable Neoprene seals and evaporator electrode connections are arranged for quick insertion of the neck of the cathode-ray tube. Typically, 12 to 20 trolleys are mounted on a large turntable so that, on rotation, the necessary power supply to the evaporator is provided from bus-bars at appropriate times in the sequence of operations. Detailed descriptions of such plant are given by Ewald (E6) and by Kennedy (K15).

To manufacture electrical resistors in the form of thin metallic films on a substrate, the best practice is probably to evaporate the alloy Nichrome on to a borosilicate glass like Pyrex which has been provided with appropriate vacuum deposited connection electrodes. Nichrome evaporates without significant change of the alloy constitution, adheres well to glass, is corrosion-resistant and provides a resistance of about 100 ohm per square for a thickness of 100 Å. Further details are given by Holland (H1). Alderson and Ashworth (AA1) have investigated the electrical and mechanical characteristics of vacuum deposited films of nickel–chromium alloy. Siddall and Smith (SS3) describe the coating by vacuum evaporation of laminated plastics with films of nickel–chromium alloy to make metal film resistors. Interest is also current in deposited nickel–iron alloy magnetic films, especially for application in electronic computer storage devices. The evaporation of gold on to quartz crystal plates to produce electrodes is described by Vigoreux and Booth (VB1), whilst the development of this technique whereby small frequency adjustments of the oscillating crystal can be made are reported by Sykes (S25) and Parrish (P11). Equipment for this purpose is marketed by Edwards High Vacuum Ltd. and by the Constantin Company. *See also* Holland (H1).

10.9. Anti-reflection and High reflection Films

By vacuum deposition of a thin layer of specific thickness of a suitable optically transparent material like magnesium fluoride on to glass it is possible to reduce the back-reflection of light from the glass and increase its light transmission. This technique is known as **blooming**. Furthermore, by the use of thin layers of other materials such as zinc sulphide and titanium dioxide on glass, the light reflection can be enhanced.

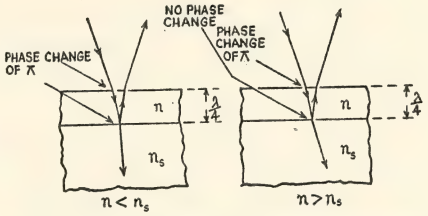


FIG. 10.10 Concerning the principles involved in single layer anti-reflection and high reflection films

To consider in an elementary way (for full theoretical accounts *see* Heavens, H19; Davy, D11; Mayer, M14) how these effects are brought about, suppose a thin uniform film of optically transparent material of refractive index n is deposited on an optically transparent substrate of refractive index n_s (Fig. 10.10). If monochromatic light of wavelength λ is incident normally on this film and the optical thickness of the film (*i.e.* nt where t is the geometrical thickness) is $\lambda/4$, then, provided that n is less than n_s, there is a phase change of π at both the air-film and the film-substrate interfaces and, moreover, the waves reflected from the air-film interface are out-of-phase by π with those reflected from the film-substrate interface. If the amplitudes of these two waves are equal in magnitude they will cancel one another by destructive interference. The condition for this equality of amplitude can be shown to be that

$$n = \sqrt{n_a n_s} \tag{10.1}$$

where n_a is the refractive index of air, taken to be unity. These refractive indices must be at the wavelength λ concerned. To obtain an ideal single layer anti-reflection film, therefore, it is necessary to deposit on glass of refractive index n_g a film of optical thickness $\lambda/4$ and of material of refractive index $\sqrt{n_g}$.

If, however, the film material has a higher refractive index than that of the substrate, a phase change of π will occur at the air–film interface but no phase change will take place at the film–substrate interface. With a film of optical thickness $\lambda/4$, therefore, the two reflected waves are in phase and so will interfere constructively, *i.e.* enhanced reflection is obtained. The reflection coefficient R at normal incidence can then be shown to be given by

$$R = \frac{(n^2 - n_a n_s)^2}{(n^2 + n_a n_s)^2}$$

For large values of R to be obtained n needs to be large.

The most effective materials for anti-reflection coatings on glass from the points of view of adherence, moisture resistance and durability are magnesium fluoride (MgF_2) and cryolite ($3NaF.AlF_3$). For glass of refractive index 1·5, n should be $\sqrt{1{\cdot}5}$, *i.e.*, 1·225. The refractive index of freshly deposited magnesium fluoride is 1·39 which decreases to 1·37 on baking in air at 300° to 400° C. The cancellation of reflection is therefore superior for glasses of higher refractive index. Cryolite is preferable, as its refractive index is smaller at about 1·34 for a durable film evacuated in high vacuum. However, the durability and moisture resistance of cryolite are inferior to that of magnesium fluoride, so the latter material is the one most widely used for blooming.

For high reflection coatings on glass, zinc sulphide of refractive index 2·37 at 5000 Å is useful, but the films are rather soft and tend to acquire a bloom. Titanium dioxide films of refractive index 2·8 at 5000 Å are preferred, as extremely hard adherent deposits are possible.

To deposit magnesium fluoride in vacuum, the type of plant described by Holland (H1) is very satisfactory (Fig. 10.11). A particular grade of magnesium fluoride prepared by British Drug Houses Ltd. is recommended, as normal grades are inclined to 'spatter' on heating in vacuum. Cryolite is also supplied by this firm. A molybdenum boat evaporation source may be used, but preferred practice is to use a radiation-heated source. A normal oil diffusion pump/rotary pump is used to produce a pressure of at most 10^{-4} and preferably 10^{-5} torr. An efficient baffle against back-streaming is necessary. The glasses or lenses to be coated are mounted on six detachable triangular metal plates with suitable holes. Ionic bombardment and subsequent heating of the glasses *in vacuo* to about 250° to 300° C by radiation are both practised to ensure highly durable coatings. For the ionic bombardment the output of a high-tension transformer is connected across the two aluminium ring-shaped electrodes shown. These electrodes are between concentric metal shields, the inner one of which is to shield the electrodes from the magnesium fluoride vapour and the outer one is to prevent overheating of the glass bell-jar. The glow discharge should be set up in air admitted via a needle valve to the system with both pumps running rather than in air at the backing pressure. After ionic bombardment cleaning the pressure is reduced as quickly as possible to 10^{-4} torr or less and the glasses then heated by radiation. The radiant heater consists of a concave metal reflector with nichrome wire spirals fitted within the top of the bell-jar. The vapour source is first heated with a shutter in place which is then removed as the deposition is begun. To obtain the optimum optical thickness of $\lambda/4$, a lamp is mounted outside an observation window in the dome of the bell-jar. The reflection of this lamp in one of the glasses or lenses is observed. The colour of the reflected image for normal incidence will be magenta for a magnesium fluoride film of optical thickness $\lambda/4$ for light of wavelength 5500 Å. Hartman (H24) describes briefly a vacuum plant in which the coating of lenses with magnesium fluoride is made automatic; the operator only has to start and stop the process.

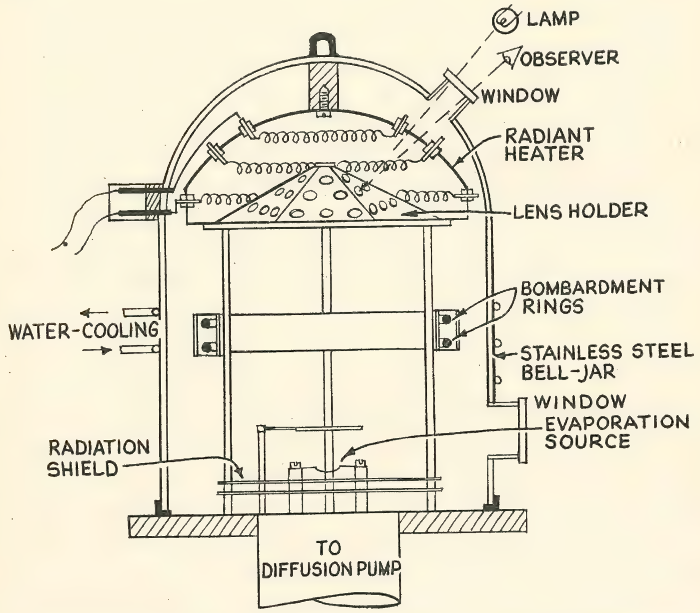


FIG. 10.11 Vacuum plant for the deposition on glasses of magnesium fluoride films (*after Holland*)

The production of high reflection layers of titanium dioxide on glass is best carried out by the method due to Hass (H21). *See also* Holland, Hacking and Putner (HHP1). Titanium metal is evaporated in vacuum from tungsten strip heated to about 2000° C by the direct passage of electric current. The residual pressure in the chamber must be 10^{-5} torr or less. The titanium film on glass is then heated to 400° to 450° C in air to oxidize it to the rutile form of titanium dioxide. The thickness of the dioxide film can be controlled by the baking time in conjunction with the deposition time for the titanium.

The technique of blooming using magnesium fluoride single layers on glass is particularly valuable when a number of glass–air interfaces are involved in a compound lens such as that of a camera. Not only is the light transmission improved, reduction of back reflections result in considerably improved contrast in the optical image, particularly noticeable in photographs taken with a camera having a three or four component lens. The enhanced reflection films are valuable in beam-splitter devices. The strongly adherent, almost optically neutral, titanium dioxide film on glass is particularly useful for this purpose. Coating one side of a parallel glass plate can produce a reflectivity of more than 40% with much less absorption of light than if a semi-transparent metal film is used.

The techniques of producing multi-layer anti-reflection and enhanced reflection layers and also interference filters are discussed in detail by Heavens (H19), Greenland (G18), Davy (D11), Mayer (M14), Cox, Hass and Rowntree (CHR1), Auwärter (A13), Tolansky (T7) and Holland (H1). These more advanced techniques require careful control in deposition to obtain optimum results. For two-layer anti-reflection coatings a combination of magnesium fluoride on titanium dioxide is preferred. As many as seven and even nine alternate layers of cryolite (as a low refractive index material) and titanium dioxide (as a high index material) have been used to achieve enhanced reflection coatings with a reflectivity of 80% or more. Interference filters capable of passing only a narrow band of light in the visible or infra-red region of the spectrum at various prescribed mean wavelengths are based on a dielectric film sandwiched between two metal films on glass (the action being that of the Fabry–Perot interferometer) or on an all-dielectric multi-layer combination.

Greenland (G19) has reviewed methods of measuring the thickness of thin films. Weinstein (W11) has given an account of the mathematical theory of multi-layer thin film filters.

10.10. Cathodic Sputtering

Typical plants for cathodic sputtering are shown in Fig. 10.12. Fig. 10.12(*a*) represents a readily constructed small plant suitable for routine laboratory use; Fig. 10.12(*b*) illustrates the small plant (Model S5) marketed by Edwards High Vacuum Ltd. The cathode is of the metal which is to be sputtered or, if expensive metals like gold, platinum and palladium are concerned, it may be a heavily electroplated base metal, *e.g.* of steel. The gas pressure for sputtering is between 10^{-2} and 10^{-1} torr (Bacquet, B32, recommends optimum pressures of 2×10^{-2} to 10^{-1} torr depending on the gas atmosphere). Across the cathode and the anode, which is the steel base-plate of the chamber, is maintained a steady p.d. of 1 to 2 kV. The positive ions created in the discharge impinge on the cathode and release from it atoms of the cathode metal. These metal atoms then travel to the substrate to be coated, which is supported beneath the cathode. In the apparatus of Fig. 10.12(*a*), the lead to the cathode is shielded by a glass tube to prevent a discharge from it and a cylindrical glass shield is placed round the cathode and substrate region. Metal supports are of aluminium, which does not sputter significantly. In the S5 plant (Fig. 10.12(*b*)) the cathode is supported on insulators connected to the underneath of the top metal cover plate. Glow discharge from the top cathode face to the cover lid is avoided by making the clearance between these two less than the length of the cathode dark space.

Primitive practice is to sputter in the residual vacuum created by a mechanical rotary pump. Much preferred practice is to exhaust the chamber to a pressure of 10^{-4} torr or less by a diffusion/rotary pump combination and then admit gas to the appropriate pressure via a needle valve. Noble metals may be sputtered in air without difficulty due to oxidation; the best choice of gas in all cases is, however, argon in which the sputtering rate is high. To minimize contamination of the argon atmosphere by desorbed gases during the sputtering, the pump should have a fairly high speed and the required pressure maintained by a continuous inlet of argon through the needle valve; the setting of a baffle valve on the vapour pump can also be used to control the gas flow. For the 24 cm dia S5 plant, a silicone oil diffusion pump with a baffled speed of about 50 litre per sec is recommended, but a two-stage rotary pump only will serve provided the chamber is flushed with gas before sputtering is begun. For large sputtering plants, the required speed at the intermediate pressure of 10^{-1} to 10^{-2} torr is best provided by a booster type vapour pump.

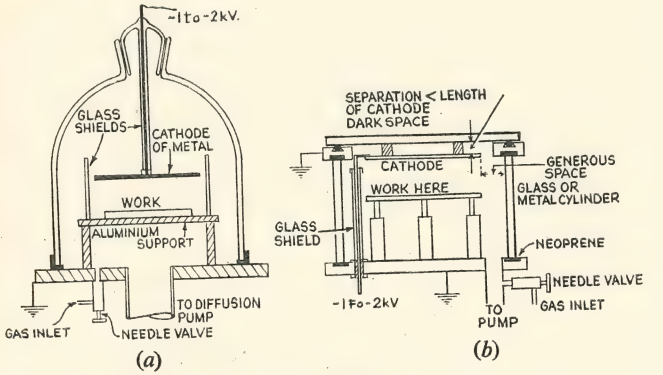


FIG. 10.12

(*a*) A laboratory unit for sputtering
(*b*) The Edwards High Vacuum Ltd. S5 sputtering plant

For sputtering, a 2 kV d.c. supply with a current of about 0·5 to 1 mA per sq cm of cathode area is satisfactory; thus the current is best at about 200 mA for a cathode diameter of 20 cm.

According to Güntherschulze (G20) for a plane-parallel cathode and anode, less sputtered deposit is obtained at the edges of a substrate placed between these electrodes because metal is lost by side diffusion. The coating uniformity is therefore improved as D/d is increased, where D is the cathode diameter and d is the separation between the cathode and the substrate.

Below a critical voltage V_c of about 400 to 500 V sputtering is insignificant, but for voltages V greater than V_c the rate of deposition, S, is related to the current density i by the equation

$$S = ki(V - V_c) \tag{10.2}$$

where k is a constant depending on the cathode metal, the cathode–anode separation, the gaseous atmosphere and the gas pressure. Much higher voltages than the recommended 2 kV therefore lead to an increased sputtering rate, but are inconvenient in practice except in large plants in which V may be as much as 10 kV. For such large plants, water-cooled cathodes are used.

Güntherschulze (G20) gives the rate of sputtering for various metals in a hydrogen atmosphere where a water-cooled cylindrical cathode of area 7 sq cm was used and the applied voltage was 850, the cathode fall of potential being 770 V. His figures in milligram of metal per ampere-hour are: Bi, 1470; Te, 1200; As, 1100; Tl, 1080; Sb, 890; Ag, 740; Au, 460; Pb, 400; Zn, 340; Cu, 300; C, 262; Sn, 196; Fe, 68; Ni, 65; W, 57; Co, 56; Mo, 56; Mn, 38; Cd, 32; Al, 29; Cr, 27; Ta, 16; Mg, 9.

Considerably faster rates are obtained in the heavier gas, argon. Bacquet (B32) gives qualitative results for the speed of sputtering of various metals in various gases (Table 10.2).

TABLE 10.2

Gas	Speed of sputtering in decreasing order
Air	Pd, Au, Ag, Pt, Cu, Cd, Ni, Fe, Al, Mg
Nitrogen	Ag, Au, Pt, Pd, Cu, Ni, Fe
Argon	Cd, Ag, Pb, Au, Cu, Pt, Ni, Fe, Zn, Si, Al, Mg
Hydrogen	Ag, Au, Pb, Zn, Cu, Fe, Ni, Co, Mo, Mn, Cd, Al, Cr, Ta, Mg

These results show that, for practical purposes, aluminium and chromium have insignificant sputtering rates; aluminium is consequently often chosen as a constructional metal where sputtering is to be avoided.

Those metals which sputter readily are gold, silver, platinum and palladium. With the exception of silver, these metals are somewhat difficult to evaporate in vacuum, so that sputtering of metals is most concerned in practice with the noble metals.

For platinum or gold in an argon atmosphere and using a 20 cm dia cathode, a p.d. of 2 kV and a discharge current of 200 mA, an opaque film can be readily produced on a substrate in about 15 min.

Plastic substrates can be coated with metals by sputtering; in this case, a water-cooled cathode is essential to avoid overheating and high pumping speed (*e.g.* by a booster pump) is demanded, especially for large plant.

The theory of the sputtering mechanism is complex and not fully understood; the most notable exponent of the science is Güntherschulze (G21); accounts of the theory are also given by Massey and Burhop (MB2) and by Holland (H1).

An important application of sputtering is the production of gold or silver films on a wax master in gramophone record reproduction. The electrically conducting film produced is used for subsequent electro-deposition copy making.

Sputtered films of gold are prepared in the manufacture of some types of metal rectifiers, barrier layer photocells and quartz crystal oscillators, but vacuum evaporation is a strong rival in these cases. Sputtered platinum films on glass and ceramics are valuable for making electrical contracts; a platinum film deposited on a borosilicate glass can be subsequently sintered by baking to within about 20° C of the glass flow point to produce an extremely tough, adherent film.

10.11. Reactive Sputtering

This term (introduced by Veszi, V4) is used to describe the technique whereby films of metal oxides on substrates can be prepared by the cathodic sputtering of a metal in a glow discharge within a gas containing oxygen. It is also possible—though not yet applied to any extent—to include other gases than oxygen in the discharge and so deposit films of hydrides, sulphides and nitrides, for example.

The technique which has been most widely practised is to sputter the metal cathode in an atmosphere consisting of a mixture of an inert gas and about 5% oxygen at a total pressure of about 10^{-1} torr. It is also possible first to sputter the metal cathode in an oxygen atmosphere so that the cathode surface becomes oxidized; subsequent sputtering of the molecules of the metal oxide is then in an inert gas. Argon is usually employed as the inert gas.

In reactive sputtering to form films of metal oxides, it is probable that three processes occur (Holland and Siddall, HS5): (*a*) an oxide layer forms on the cathode due to bombardment with oxygen ions; the molecules of the metal oxide are then released by subsequent ion bombardment; (*b*) the sputtered metal atoms absorb oxygen from the gaseous atmosphere during their paths to the substrate; (*c*) the metal atoms absorb oxygen as they condense on the substrate. Which one of these three processes predominates will depend on the cathode metal, the cathode temperature, the substrate temperature and the partial pressure of oxygen in the residual gas.

A wide range of metals can be sputtered reactively to produce a thin film of the corresponding oxide, *e.g.* aluminium, beryllium, bismuth, cadmium, cerium, copper, indium, iron, lead, magnesium, molybdenum, nickel, platinum, silicon, tantalum, tellurium, thallium, thorium, tin, titanium, tungsten and zinc. In most cases these films are strongly adherent to a glass substrate. The state of oxidation of the film can be controlled in many cases depending on the partial pressure of the oxygen in the sputtering atmosphere. This is particularly useful when it is required to produce an excess of metal atoms in the deposited oxide film so as to obtain higher electrical conductivity than for the normal oxide, *e.g.* cadmium sputtered in an atmosphere containing a high percentage of oxygen will form electrically insulating fully oxidized cadmium films; if the oxygen concentration is reduced, excess cadmium atoms in the oxide film render it conducting.

Metal oxide films can be prepared by direct evaporation in vacuum but difficulties often arise due to chemical reaction between the oxide and the heater material and dissociation of the oxide on heating in vacuum. An inert heater metal like platinium can be chosen to avoid the former disadvantage. A sub-oxide or the metal itself may be evaporated and the film formed then oxidized by heating in air, as in the cases of silicon monoxide to give silica and titanium to give titanium dioxide, but the range of metals for which this is possible is considerably less than that which can be reactively sputtered.

The design of plant for reactive sputtering is basically similar to that for sputtering metallic films (§ 10.10), but the following important additional points need to be considered (Holland and Siddall, HS5):

(1) Reactively sputtered oxide films a quarter of a wavelength thick can be prepared in 2 to 5 min provided a p.d. across the cathode and anode of about 3 kV and with a discharge current density of 5 mA/cm^2 is used. In some cases, *e.g.* aluminium oxide and titanium oxide, three of four times this current density is required. To prevent undue heating of the cathode it is desirable, therefore, to water-cool it. Purity of the cathode metal is important.

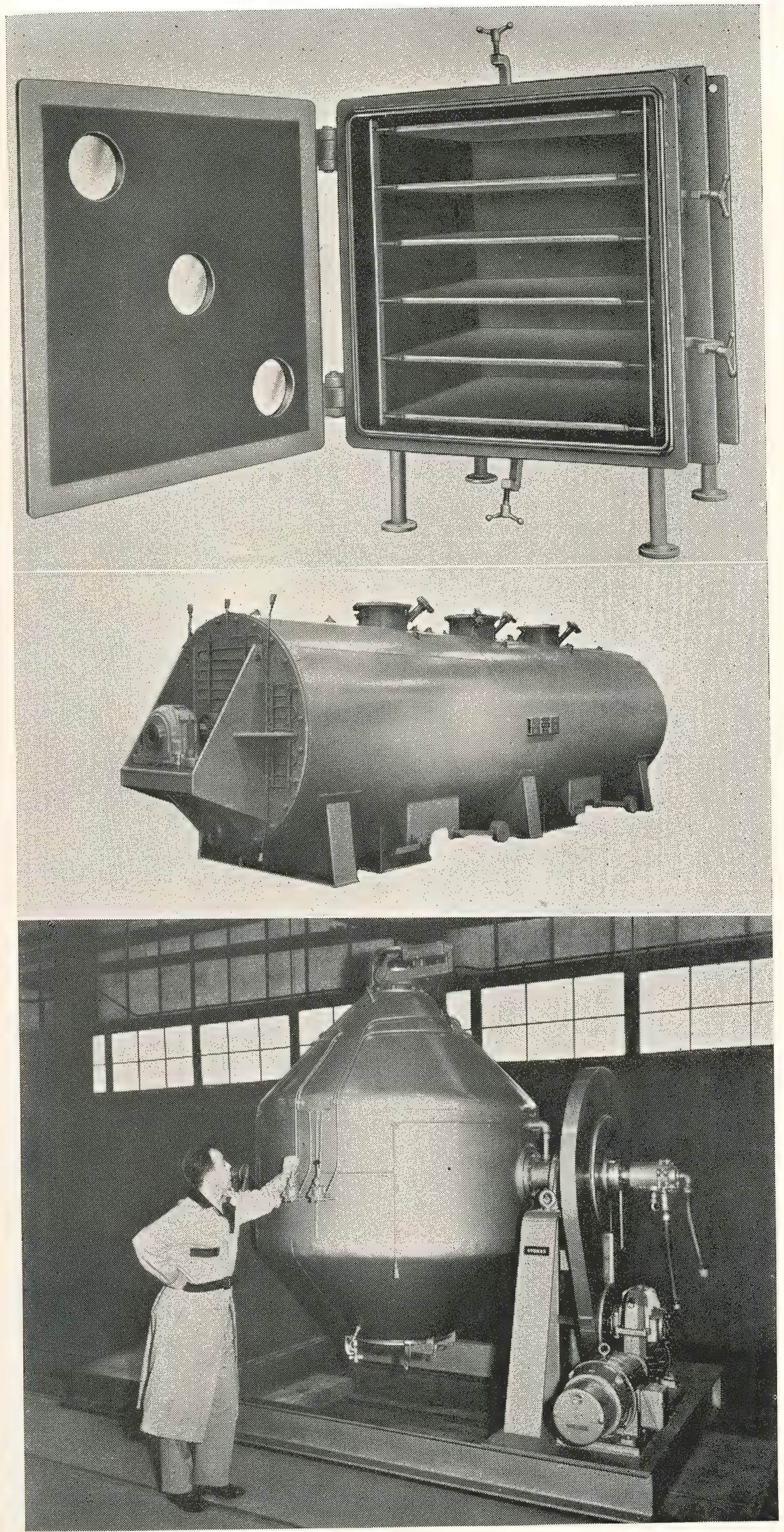
(2) The transformer of the single-phase rectifier circuit used for the power supply should have poor regulation, *i.e.* its secondary winding reactance should increase as the load current rises, or a choke should be inserted to ensure this; otherwise, at the high-discharge current densities necessary, undesirable transition of the normal discharge to an arc may occur.

(3) The appropriate argon–oxygen gas mixture is best prepared in an auxiliary reservoir which contains a drying agent, *e.g.* phosphorus pentoxide in a trap, to ensure that water vapour (which will dissociate to hydrogen and oxygen in the discharge) is removed.

(4) The vapour pump should provide high pumping speed at the intermediate pressure range of 10^{-2} to 10^{-1} torr, otherwise contamination of the sputtering atmosphere by gas and vapour desorbed from the chamber walls will take place. For large plants, a booster-diffusion pump is preferred. The rate of inflow of the argon–oxygen gas mixture into the sputtering chamber is controlled by a needle valve in conjunction with the setting of the baffle-valve on the vapour pump.

These points are considered in the design of plant shown in Fig. 10.13, which is based on that published by Holland and Siddall (HS5). Note the use of two valves in parallel between the gas reservoir and the sputtering chamber: one is a needle valve to regulate the inlet gas flow; the other is a larger isolation valve which is opened to evacuate the auxiliary chamber before the gas mixture is admitted from the supply cylinders.

The chief applications of reactively sputtered oxide films have been to the preparation of electrically conducting, optically transparent layers on glass and other insulating materials. In some cases the oxide film alone is used, in others, a film of metal is deposited on to an appropriate oxide layer on the insulating substrate; thirdly, metal films sandwiched between oxide films on a substrate have been used.



Courtesy of F. J. Stokes Corp.

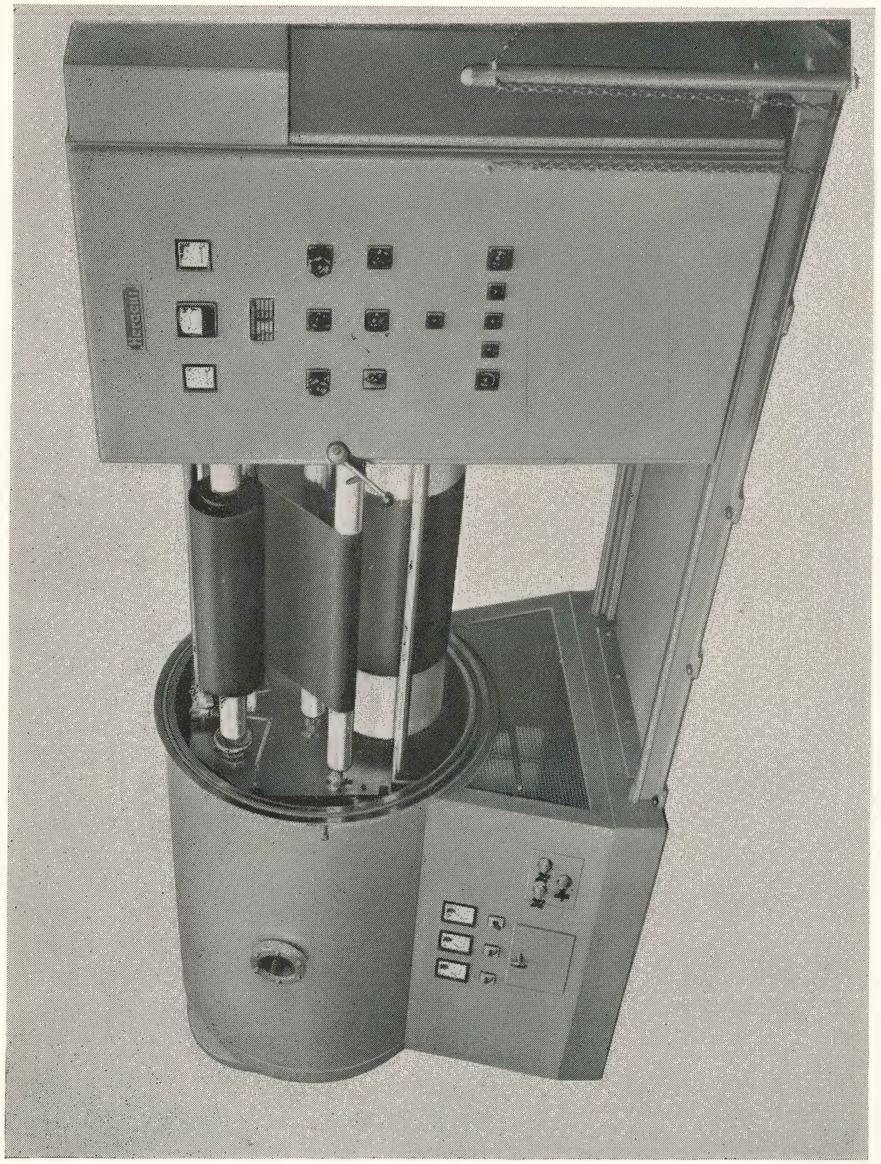
Plate 7

Top: shelf drier; the manifold connections to the vacuum pumps are outside the chamber at the rear; shelf sizes in range from 24 × 24 in. up to 44 × 40 in. *Centre:* rotary drier; sizes range from 20 in. to 30 ft in length and 15 in. to 5 ft in diameter. *Bottom:* conical rotating drier; charged via a hinged cover, discharged via a port with a self-wiping, quick-acting, vacuum-tight valve actuated by a worm gear; working capacities from 3 to 150 cu. ft (*see* p. 414).

Plate 8

Vacuum plant for drying a roll of material

The material is wound off a heated drum within an evacuated steel chamber. The chamber and the drum are heated by the circulation of a liquid which is raised to a regulated temperature by electrical heating. A double motor drive enables the velocity of the band of material to be controlled. Pumping is by means of a Roots pump backed by a two-stage gas ballast rotary pump (*see* p. 415).



Courtesy of W. C. Heraeus GmbH.

Early work on the reactive sputtering technique and on the preparation of conducting films of gold on bismuth oxide on glass is due to Preston (P12) Gillham and Preston (GP1), and also to the Libbey–Owens–Ford Glass Company (*Brit. Pat.* 682,264). Gillham and Preston report that very thin gold films (*e.g.* 60 Å) sputtered directly on to glass have much higher resistivity than the bulk metal and that the optical absorption is greater than would be expected from calculations based on the bulk optical constants. These properties are influenced by the cleaning of the glass; cleaning with dry precipitated chalk tends to result in gold films of lower resistance and absorption. If, however, the gold film is sputtered on to a reactively sputtered film of bismuth oxide on glass, the film has a pale yellow colour and, moreover, subsequent heating for a few minutes to about 200° C provides resistance and optical absorption properties close to that of the bulk metal. The reason for this is that bismuth oxide favours adhesion and minimum aggregation of the superimposed gold. A gold film 60–70 Å thick on a film of bismuth oxide 100 Å thick on glass, after heating, had a resistance of 10 ohm per square and an optical transmission of 70% (for tungsten filament light at a colour temperature of 2700° K). Other substrates than bismuth oxide could be used; some, like zinc oxide, resulted in an opposite effect of providing a film of exceptionally high resistance. A further layer of bismuth oxide may be deposited on to the gold film and the three-layer sandwich again heated in air to 225° to 250° C, guaranteeing good adhesion and stability.

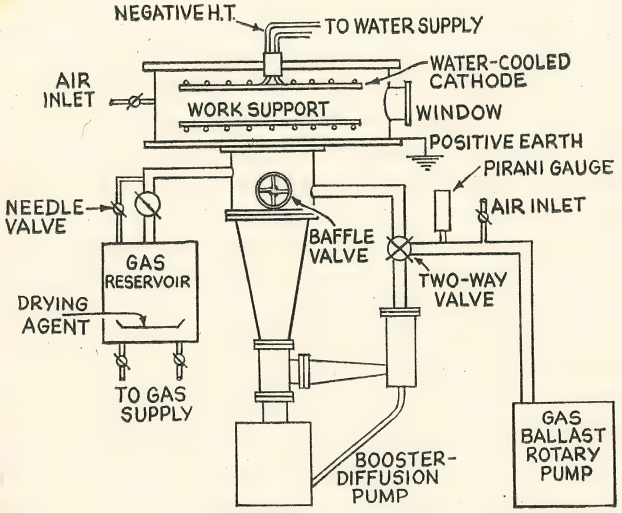


FIG. 10.13 Outline of arrangement of a plant for reactive sputtering

This development has led to the availability of glass for aircraft windows which can be de-misted and de-frosted by heating. The provision on the glass of the conducting layer with a resistance of 10 ohm per square and an optical transmission of 75% means that a window of area 1 sq ft can have 1 kW of electrical power dissipated in it by the application across electrodes placed on opposite edges of a p.d. of 100 V; this power is ample for de-frosting purposes. These films also have high infra-red reflectance and may therefore be used as transparent heat reflecting coatings. Gold–bismuth oxide coated glass is supplied in Britain by Megatron Ltd.

Ennos (E7) has prepared highly conducting gold films by *evaporation* in vacuum of the metal on to *evaporated* bismuth oxide and shows that they compare favourably with deposits formed by sputtering.

Conducting layers on insulators have also been made by the reactive sputtering of cadmium oxide, tin oxide, indium oxide and iron oxide. Holland and Siddal (HS6) give a valuable survey of this work and have also investigated the effect on the resistivity and stability of the films of the following parameters: variation of the volume per cent of oxygen in the sputtering atmosphere over the range from 5 to 100, the other gas being argon; the effect of the temperature of the substrate during deposition; the effect of subsequent heat treatment of the film in air. To prepare, on glass, cadmium oxide films about 650 Å thick with a resistance of 100 ohm per square and an optical transmission of 60% (at 5500 Å), the volume percent of oxygen in the discharge was 5% and a sputtering time of 20 min was necessary with a 45 cm dia cathode at 10 cm from the substrate, the anode–cathode p.d. being 3 kV and the discharge current density 0·3 mA/sq cm. The films were stabilized by heating to 400° C in air. For double this thickness, a transmission of 85% and a resistance of 75 ohm per square were obtained. As cadmium oxide is attacked by moist air, a protective coating of lacquer is desirable. Cadmium oxide coated glass is supplied by Megatron Ltd.

Tin oxide films prepared by reactive sputtering have high resistivity and have not been used commercially. Megatron Ltd. supply indium oxide coated glass with an optical transparency of 80% and a resistance of 2000 to 3000 ohm per square. Holland and Siddall (HS6) report that the best results were obtained in the reactive sputtering of indium oxide when the cathode temperature approached the melting point of indium (155° C). They produced the films in a 50/50 oxygen–argon gas mixture. On heating the film to 400° C in air it became non-conducting because of complete oxidation of the excess metal. Iron oxide was reactively sputtered in a 30 volume per cent hydrogen–oxygen mixture, but the preparation of iron oxide films is best by vacuum evaporation at 10^{-3} torr and subsequent baking of the film in air (Holland, Moutou and Hacking, HMH1). Iron oxide films deposited on glass and then baked are very hard and stable; they have been used as light absorbing media for tinting spectacle lenses.

Conducting metal films of gold on bismuth oxide and of cadmium oxide are also used on some types of electrical measuring instrument glass windows to prevent the formation of electrical charges; Preston (P12) and Veszi (V4) have used cadmium oxide in place of gold films on selenium photocells to give improved efficiency and light sensitivity over a wider range in the spectrum.

11

VACUUM DRYING AND FREEZE-DRYING

11.1. Introduction

Almost every other material we encounter in daily life has been subjected to some dehydration process. To mention only a few, there are coal, foundry sand, cement, paper, several kinds of processed foodstuffs, tobacco, textile fibres, sugar and many chemicals and pharmaceutical products (Rumford, R21).

In a modern paper on drying processes (MacTaggart, M16) sixteen methods for removing moisture from materials are enumerated, two of which employ vacuum but not high vacuum. Water may occur in the cavities in materials, it may be adsorbed on the surfaces of individual particles, it may be combined chemically or physically with the solid material, or it may even form the bulk of the substance to be dried, as in the cases of peat or a solution of a solid in water.

In all cases where water has to be removed by evaporation, as distinct from its removal by mechanical means like pressing or centrifuging, the latent heat of vaporization has to be supplied to the material. For every gram of water removed at a temperature near the freezing point, this energy requirement is of the order of 600 gram-calories (one international gram-calorie = 4·186 joule), corresponding to about 1000 B.t.u. per pound. These are the minimum energy requirements; it makes no difference whatever in which way the necessary evaporation process is performed, be it by contact heating, by radiant heating, by high frequency heating (Stephens, S26) by driving the water vapour from the surface by a hot air blast, or by drawing it away by suction by means of a vacuum pump (Flosdorf, F10; Neumann, N10). In addition, there will be energy losses in the machinery employed; the overall efficiencies, defined as the ratio of the energy employed in supplying the latent heat of vaporization of the water to the total energy required to drive the mechanism, are in the range from 25% to 75%, depending on the type of drying process. As far as the cost of the process is concerned the initial expenditure for capital equipment for vacuum drying is likely to prove higher than for other processes employing direct heating. Advantages in speed of drying are often obtained (*e.g.* the commercial drying of shellac may be 6 hours per batch by vacuum methods as against 72 hours by normal means) but it is the special properties of the final dehydrated product—not obtainable by other methods—which makes the employment of vacuum drying attractive.

11.2. The Advantages of Vacuum Drying

There are three main advantages of vacuum drying: (*i*) the almost complete absence of air; (*ii*) the material to be dried may be maintained at low temperature; (*iii*) the dehydrated product is usually much more easily dissolved than that obtained by other methods, *e.g.* heating.

A consequence of (*i*) is that vacuum drying is valuable for materials which deteriorate by oxidation or are chemically altered on exposure to air at normal temperatures; as a result of (*ii*) materials which would decompose or be otherwise altered at higher temperatures may be dried and, in the case of particularly labile substances, *e.g.* many pharmaceutical products, the material may be frozen during drying, *i.e.* **freeze-drying** is concerned.

Vacuum drying is also useful when the solvent (other than water) concerned is sufficiently valuable to make it worthwhile for it to be recovered during the process.

The ready solubility of vacuum-dried products may be illustrated by a comparison of two methods of drying gelatine solution. If it is heated to dry it, the solution will become increasingly viscous to be eventually converted into a horn-like substance which can only be dissolved in water with extreme difficulty; in fact, solution can only be obtained after prolonged soaking on account of the smallness of the accessible 'inner surface' which can only be reached by slow diffusion. In the case of desiccation under vacuum from the frozen state, *i.e.* freeze-drying, the gelatine solution is first made into a foam by the introduction of air or carbon dioxide. This increases greatly its effective surface. It may then be spread out in a flat dish to form a layer a few millimetres in thickness. This dish is then cooled to about −10° C and introduced into a vacuum chamber in which a residual air pressure of a few hundredths of a torr can be maintained. The effect of first freezing the solution is to reduce the thermal motion of the molecules so much that coalescence becomes impossible. The vapour pressure of water (ice) at −10° C is about 2 torr (Table 11.1). The water vapour will therefore diffuse out of the solid cake of gelatine into the vacuum where it is pumped away. An extremely porous structure with a large accessible surface remains, which is readily soluble without soaking.

11.3. Problems in Vacuum Drying

The variation of the vapour pressure of water with temperature is of fundamental concern in vacuum drying. This is shown in Table 11.1 together with the moisture content of one litre of saturated air at various temperatures.

Many materials may be vacuum-dried at room temperature or the temperature may be raised to accelerate the rate of release of water vapour. Labile substances must usually be freeze-dried. In this last case, sublimation from ice to water vapour takes place. The residual gas pressure required in the vacuum chamber must be significantly less than the vapour pressure of water at the temperature concerned to ensure ready passage of the water molecules from the product to the collecting device used. These vacuum requirements are considered later.

TABLE 11.1

Water vapour pressure and moisture content of saturated air at various temperatures

Temp., °C	Water vapour pressure, torr	Moisture content, mg/litre
100	760	
80	355	
60	150	
40	55·3	
20	17·5	17·3
0	4·6	4·8
−10	1·95	2·14
−20	0·77	0·88
−24	0·52	
−28	0·34	0·41
−30	0·28	0·33
−34	0·185	
−36	0·15	0·178
−38	0·119	
−40	0·093	0·117
−44	0·058	0·074
−50	0·029	0·038
−60	0·007	0·011
−70	0·002	0·003
−80	0·0004	0·0008

Problems that arise in all cases of vacuum-drying and freeze-drying are:

(*a*) *Means have to be provided for the continuous disposal of water vapour without contaminating the vacuum pump.* Note that 1 gram of water vapour at a pressure of 10^{-1} torr has a volume of about 10,000 litres. If a rotary pump is used, it is bad practice to let the water vapour dissolve in the pump oil and then remove it by heating the oil (§ 2.6) because this causes loss of valuable volatiles from the oil which are needed for satisfactory lubrication of the pump mechanism.

(*i*) The simplest way of disposing of moisture is to use hygroscopic substances as absorbents. Some of the best known are listed in Table 11.2. The most efficient absorber is seen to be phosphorus pentoxide (3 gram of P_2O_5 absorb 1 gram of water approx); it is frequently used in small freeze-drying plants (§ 11.6) and for general purpose vacuum systems between the backing pump and the vapour pump (§ 1.1). It is rather expensive and cannot be regenerated. The next best practicable material is activated alumina (Al_2O_3), which is used to some extent as a desiccant in big production plants. As it can be regenerated by heating, it is possible to use it in a continuous drying cycle in which two packed tubes or towers of the alumina are available to be inserted alternately between the tank and the pump, *i.e.* the one not in use is undergoing regenerative baking. The packing and cross-section of the drying towers have to be adjusted to create the minimum possible impedance to gas flow. Such regenerative towers are obtainable on the market (*e.g.* from the Kestner Evaporator and Engineering Company).

Comparison of Tables 11.1 and 11.2 is of interest, as it shows the temperatures at which the moisture content of air is equal to the residual water per litre of dried air produced by a particular desiccant. These temperatures are −60° C for silica gel and for anhydrous $CaSO_4$, −70° C for anhydrous $Mg(ClO_4)_2$ and for Al_2O_3, and −80° C for P_2O_5.

TABLE 11.2

Comparative efficiencies of various dehydrating agents (Bower, B33)

Material	Litres of air having moisture content of 20 mg/litre which can be dried by one ml of desiccant	Residual water per litre of dried air, mg
$CuSO_4$ (R) (anhydrous)	0·45 to 0·7	2·7 to 2·9
$CaCl_2$ (granular)	6·1 to 24·2	1·4 to 1·6
$CaCl_2$ (tech. anhydrous)	4·0 to 5·8	1·23 to 1·27
$ZnCl_2$ (sticks)	0·8 to 2·1	0·94 to 1·02
$Ba(ClO_4)_2$ (anhydrous)	2·3 to 3·7	0·76 to 0·88
NaOH (sticks)	2·3 to 8·9	0·78 to 0·83
$Mg(ClO_4)_2.3H_2O$	4·0 to 7·2	0·028 to 0·033
KOH (sticks)	3·2 to 7·2	0·010 to 0·017
Silica gel (R)	2·1 to 5·2	0·002 to 0·01
$CaSO_4$ (R) (anhydrous)	1·2 to 18·5	0·004 to 0·006
CaO	7·6 to 10·1	0·003 to 0·004
$Mg(ClO_4)_2$ (anhydrous)	2·8 to 5·9	0·0016 to 0·0024
Al_2O_3 (R)	5·6 to 6·8	0·0008 to 0·0012
BaO	10·6 to 25	0·0006 to 0·0008
P_2O_5		0·00005

(R) means that the desiccant can be regenerated by heating to over 100° C

When using dessicants in the form of powders (*e.g.* phosphorus pentoxide) care must be taken to prevent fine particles of the powder from being sucked into the vacuum line. These would not only disturb the functioning of the pump by accumulating absorbed water but would, in some cases, eventually damage or corrode the mechanism of a rotary pump. For example, phosphorus pentoxide becomes corrosive phosphoric acid, and alumina and some other desiccants are abrasives.

(*ii*) If the dehydration requirements are not too stringent, liquid absorbents for water vapour, like hygroscopic lithium chloride and lithium bromide solutions, may be used instead of solid desiccants. A 60% solution of lithium bromide in water has a vapour pressure of about 1 torr at 10° C, whereas an ice surface would need to be kept at about −20° C in order to have the same vapour pressure (Table 11.1). Lithium bromide is extremely hygroscopic and thus removes water vapour from the surrounding air. In use, it is continuously circulated so that the water vapour can be driven from it by heating in a part of the apparatus remote from the drying chamber containing the

material undergoing desiccation. After cooling, the lithium bromide solution is then again returned in the cycle to the drying chamber. Such systems are used in air-conditioning plants and, in principle, are heat-operated absorption-refrigeration units. The method is also occasionally used in vacuum desiccation, but is not of special interest from the standpoint of vacuum technique proper (Tucker and Sherwood, TS1).

(*iii*) A cold trap can be arranged between the tank and the pump. If this trap is at, *e.g.* −70° C, then ice formed on the condensing surface of the trap will have a vapour pressure of about 2×10^{-3} torr (Table 11.1).

(*iv*) A gas-ballast pump can be used (§ 2.5).

No special difficulties are encountered in vacuum drying if the substance can be dehydrated at residual air pressures of 10 to 30 torr (*i.e.* at and above the region of the vapour pressure of water at room temperature, the product to be dried being at room temperature or slightly heated). This is especially true of larger plants for the concentration by vacuum drying of fruit juice, where two- to four-stage steam ejectors may be used so that the water vapour removed from the product has no deleterious influence on the pump (Schwarz, S27; Schwarz and Penn, SP1).

(*b*) *Means for the liberation of water vapour from the material to be dried have to be provided*, especially for substances having small interstices between the particles, like fine powders or tightly packed solid sheets (*e.g.* paper capacitors), without damaging the product by heating it to above 100° C.

(*c*) *A method has sometimes to be provided for maintaining the temperature of the surface*, e.g. *a liquid solution, constant*, in order to avoid it reaching so low a temperature, due to loss of heat of evaporation of the water, that the vapour pressure of the water drops so much that the speed of drying is reduced seriously.

Heating of the material by steam, hot water, hot oil, or Dowtherm* or electric heating is practised in cases where non-heat-sensitive materials are to be handled in large vacuum shelf driers, rotary vacuum driers and rotating vacuum driers (§ 11.4). Another useful procedure for achieving (*b*) and (*c*) is to use infra-red radiation heating to the material surface (Kestner Evaporator and Engineering Company) or high frequency dielectric heating of the bulk of the material (Redifon Ltd.). In handling large qualities of liquids, it has been found practical to introduce them in the form of thin films in the drier (Dixson, D14) or to use continuous moving belts (Hellier, H25) (§ 11.4).

11.4. Vacuum Drying Systems

The principles of six representative types of vacuum drying systems are schematically illustrated by the diagrams of Fig. 11.1.

Fig. 11.1(*a*) shows the only arrangement in which a condenser or trap is unnecessary between the chamber and the pump. This utilizes a steam ejector pump which handles both the air and the water vapour released.

For dehydration under rough vacuum conditions, and especially where the material to be dried may be heated to between 20° C and 10° C, a water-cooled surface condenser (Fig. 11.1(*b*)) is often employed between the chamber and the pump, which is a rotary pump of the gas-ballast type or one with an auxiliary oil clarifier. In a typical vertical tube surface condenser (Fig. 11.2) the water vapour from the material is pumped through a water-jacketed cylindrical tube which contains baffles to ensure effective circulation and condensation of the water vapour in the condenser. At the base is a chamber in which the condensed water collects; also provided is a stopcock for draining off excessive condensed water. This arrangement is only usually suitable for a total pressure in the chamber between 5 and 20 torr, as the vapour pressure of water (Table 11.1) is 4·6 torr at 0° C and 17·5 torr at 20° C.

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* Dowtherm $(C_6H_5)_2$, or the mixture with its oxide, is a liquid suitable for circulation in heater coils.

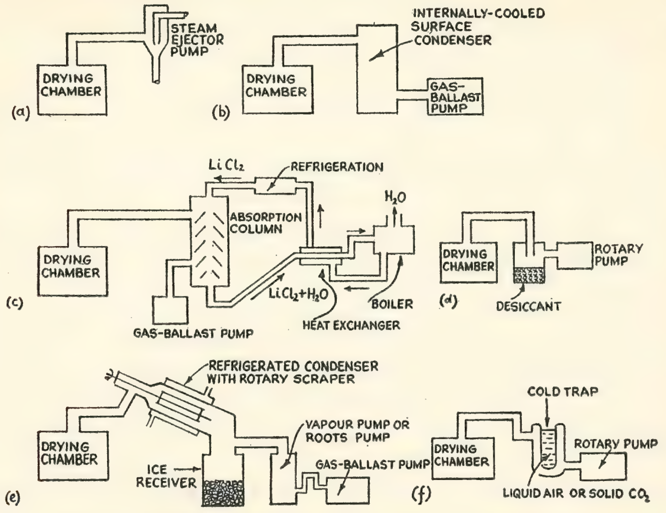

STEAM EJECTOR PUMP
DRYING CHAMBER
(a)
INTERNALLY-COOLED SURFACE CONDENSER
DRYING CHAMBER
GAS-BALLAST PUMP
(b)
LiCl₂
REFRIGERATION
H₂O
ABSORPTION COLUMN
DRYING CHAMBER
LiCl₂+H₂O
BOILER
HEAT EXCHANGER
GAS-BALLAST PUMP
(c)
DRYING CHAMBER
ROTARY PUMP
(d)
DESICCANT
REFRIGERATED CONDENSER WITH ROTARY SCRAPER
VAPOUR PUMP OR ROOTS PUMP
GAS-BALLAST PUMP
DRYING CHAMBER
ICE RECEIVER
(e)
COLD TRAP
DRYING CHAMBER
ROTARY PUMP
(f)
LIQUID AIR OR SOLID CO₂

FIG. 11.1 Six basic types of vacuum drying system

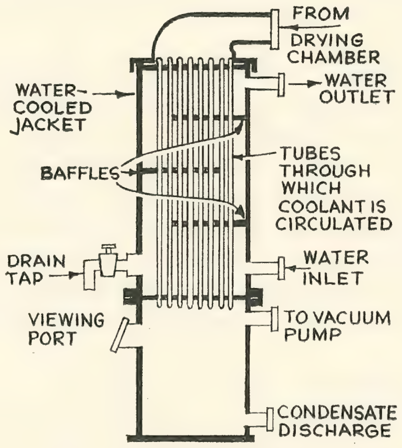

FROM DRYING CHAMBER
WATER-COOLED JACKET
WATER OUTLET
TUBES THROUGH WHICH COOLANT IS CIRCULATED
BAFFLES
DRAIN TAP
WATER INLET
VIEWING PORT
TO VACUUM PUMP
CONDENSATE DISCHARGE

FIG. 11.2 A vertical tube surface condenser

Fig. 11.1(*c*) illustrates the use of cooled lithium chloride or of brine solution as a hygroscopic agent for the removal of water vapour released on drying. Such plants are best pumped by a gas-ballast pump, operate at a total pressure of about 1 torr and can handle as much as 200 lb of water per hour if the lithium chloride is circulated continuously in a closed circuit comprising a refrigerator and the dehydration column and, furthermore, the absorbed water is boiled off.

For vacuum drying at total pressures below 1 torr and especially for **freeze-drying** (§ 11.6) at pressures down to 10^{-2} or 10^{-3} torr, the water vapour pressure must be reduced either by an effective desiccant or by a refrigerated condenser.

The use of a desiccant like phosphorus pentoxide (Fig. 11.1(*d*)) enables the total pressure to be as low as 10^{-3} torr provided the material to be dried is refrigerated. Generally such desiccants are used only in small plants, though activated alumina has been employed as a desiccant in packed towers in production vacuum drying plant.

The most effective and widely employed means of disposing of the water vapour in drying plants operated at a total pressure below 1 torr is by means of a refrigerated condenser between the chamber and a gas-ballast pump or, for pressures in the region between 10^{-1} and 10^{-3} torr, the use of a Roots pump backed by a gas-ballast pump is preferred, especially for large plants. A mechanically refrigerated condenser (Fig. 11.1(*e*)) with a conventional ammonia refrigerating machine enables temperatures of $-70°$ F ($-57°$ C; vapour pressure of ice $= 10^{-2}$ torr approx) to be attained. An alternative to mechanical refrigeration in freeze-drying practice (§ 11.6) is the use of a trap (Fig. 11.1(*f*)) filled with a mixture of solid carbon dioxide (dry ice) and methyl cellosolve (ethylene glycol monoethylester) which enables the surface of the condenser to be reduced to $-94°$ F ($-70°$ C; vapour pressure of ice $= 2 \times 10^{-3}$ torr).

The use of a mechanically refrigerated trap (*see also* § 11.5) enables 100 lb of ice or even more to be collected in the drying of a single batch. For example, recent developments in Germany (E. Leybold's Nachfolger) are towards the dehydration of as much as one ton of chicken meat in a single batch placed in trays in a very large horizontal cylindrical chamber. A large refrigerated condenser is used to collect the water vapour pumped off; the ice formed when the dehydration of the batch is complete is then melted by raising the temperature of the isolated condenser and the water is run off into an auxiliary reservoir. Pumping is by a large Roots pump backed by gas-ballast pumps.

The growth of the ice crust on the refrigerated condenser causes the effective surface temperature to increase because of the poor thermal conductivity of ice (§ 11.5). To remove the ice continuously during the drying process, a condenser with a rotary scraper may be used (Fig. 11.1(*e*)). This consists of a stationary cylindrical refrigerated trap within which is a rotating blade which scrapes off the ice formed by condensation of water vapour on the inside wall of the cylinder. A further advantage is that the ice is removable to a reservoir without interruption of the drying process.

Many types of vacuum drying chamber are used. Plate 7 illustrates the **shelf drier**, **rotary drier** and **rotating drier** (Stokes Corporation). The shelf drier is fabricated from welded steel and has a door which is closed and bolted against a fitted rubber gasket. The shelves and the top and bottom of the chamber are fitted with jackets containing internal baffles. These jackets are heated by the circulation of steam, hot water, oil or Dowtherm or may be adapted for electrical heating. Such shelf driers—available in a variety of sizes—are suitable for drying at temperatures between 0° and 100° C a considerable variety of chemicals, food extracts, glues, rubbers, explosives and certain non-heat-sensitive pharmaceutical products. A typical application reported by the Stokes Corporation is the drying of seed lac. At a maximum permissible temperature of 30° C, trays 14 in. by 40 in. were loaded to a depth of 1 in. in a test run and the moisture content was reduced from 25% to 2% in 7 hours. Pumping was by a rotary pump with a continuous oil clarifier; the shelf drier chamber was heated by hot water circulation, and a vertical tube surface condenser was fitted between the chamber and the pump.

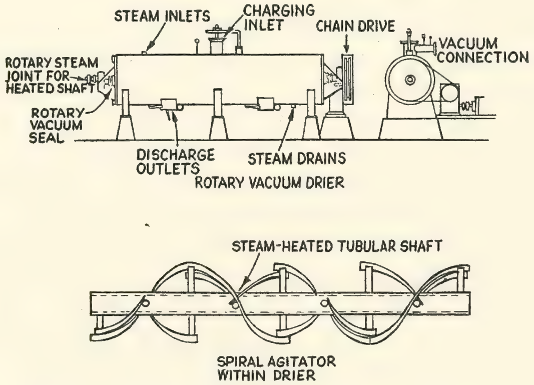

STEAM INLETS
CHARGING INLET
CHAIN DRIVE
VACUUM CONNECTION
ROTARY STEAM JOINT FOR HEATED SHAFT
ROTARY VACUUM SEAL
DISCHARGE OUTLETS
STEAM DRAINS
ROTARY VACUUM DRIER
STEAM-HEATED TUBULAR SHAFT
SPIRAL AGITATOR WITHIN DRIER

FIG. 11.3 The Stokes rotary vacuum drier

To obtain more rapid drying, constant agitation of the material is effected in the **rotary vacuum drier**. This comprises a horizontal jacketed cylindrical chamber in which an agitator is revolved continuously (Fig. 11.3). The temperature required during drying is maintained by the passage of water or oil through the chamber jacket and, for larger models, also through the central shaft of the agitator. This type of drier is usually employed for the removal of either water or hydrocarbons from wetted solids, *e.g.* plastics like cellulose acetate and cellulose acetate butyrate or metal powders wetted with hydrocarbon solvents. Hydrocarbons may be recovered at the surface condenser between the drier and the pump. From a long list of materials given by Stokes Corporation, which have been dried by such means, the following are typical: shellac, chlorinated rubber, cooked potatoes, flour, fish-meal, moulding powders, powdered metals, starches and white lead.

If the material to be dried cannot withstand the mechanical action of the agitator of a rotary drier, *e.g.* in the case of crystalline materials which must not be defaced, a rotating vacuum drier is used. The heated, jacketed cylindrical chamber itself is rotated; this chamber is fitted with herring-bone flights which give a gentle lift and fall tumbling motion to the material during drying.

The drying of a roll of material, *e.g.* paper or plastic, is conveniently carried out in plant such as that made by Heraeus GmbH (Plate 8). The jacketed cylindrical chamber is heated and the roll wound over the heated drums within the vacuum during drying. The vacuum is provided by a Roots pump with a two-stage rotary gas-ballast pump and a surface or refrigerated condenser is used, depending on the total pressure permissible and the degree of drying required.

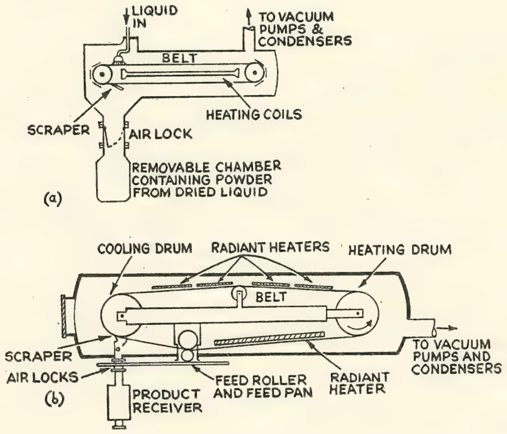

LIQUID IN
TO VACUUM PUMPS & CONDENSERS
BELT
HEATING COILS
SCRAPER
AIR LOCK
REMOVABLE CHAMBER CONTAINING POWDER FROM DRIED LIQUID
(a)
COOLING DRUM
RADIANT HEATERS
HEATING DRUM
BELT
SCRAPER
TO VACUUM PUMPS AND CONDENSERS
AIR LOCKS
FEED ROLLER AND FEED PAN
RADIANT HEATER
(b)
PRODUCT RECEIVER

FIG. 11.4 Vacuum belt driers

(*a*) After Hellier; (*b*) after Flosdorf

To provide as large as possible an area of evaporation for the drying of liquids like milk and amino-acids, a method of handling large quantities (200 lb of water per hour) is by means of the **belt drier** (Hellier, H25). The procedure is to concentrate the solution and then spray it continuously on to a moving belt in a horizontal evacuated vessel (Fig. 11.4). Heating coils between the horizontal sections of the continuous belt are used to boil off the water at a maximum temperature of 40° C (water vapour pressure = 55 torr). Dried material which clings to the underside of the moving belt is scraped off and collected in an auxiliary chamber connected to the main drying chamber via an air lock.

The necessary vacuum and collection of water vapour is provided by one of three methods already described: (*i*) a rotary gas-ballast pump providing a pressure of 10^{-3} to 5×10^{-1} torr and a condenser with rotary scraper; (*ii*) a gas-ballast pump and lithium chloride or brine absorption column, the total pressure being 5×10^{-1} to 4 torr; (*iii*) steam ejectors to provide a pressure of about 1 torr.

11.5. Mechanically Refrigerated Cold Traps

A mechanically refrigerated condenser and one with a rotary scraper are shown in detail in Figs. 11.5(*a*) and (*b*) respectively.

The capacity of a refrigerating unit is often quoted in 'tons of refrigeration'. According to this commercially used nomenclature, 'one ton of refrigeration' is the quantity necessary to convert one ton of water at 32° F (0° C) into ice at 32° F within 24 hours, corresponding to 318,000 B.t.u. in 24 hours or 13,250 B.t.u. per hour. On the Continent, the practical unit employed is the 'frigoria hour', which is equal to 4 B.t.u. per hour (Miller, M17).

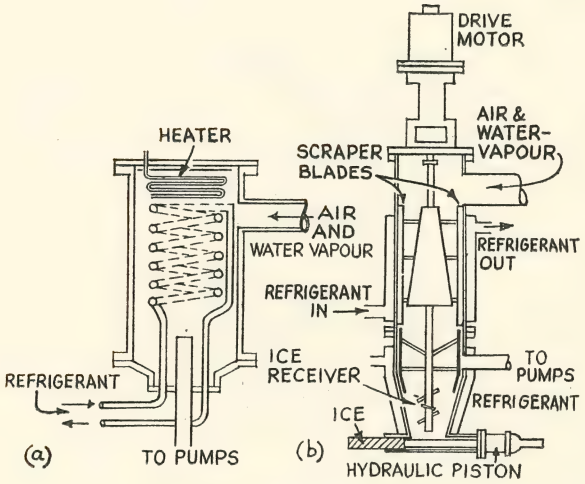


FIG. 11.5

(*a*) A mechanically refrigerated condenser
(*b*) A refrigerated condenser with rotary scraper

The object of the rotary scraper (Morse, M18; National Research Corporation: Brit. Pat. 586693, 1947; applicant W. W. Triggs) is to limit the thickness of the ice crust formed during the drying process to a maximum of about 0·2 to 0·4 mm so as to prevent undue increase of the effective temperature of the refrigerated surface because of the poor thermal conductivity of the ice which forms (the thermal conductivity of ice is 5×10^{-3} cal cm^{-1} sec^{-1} °C^{-1}, *i.e.* about 5% of that of mild steel).

The model illustrated is for quantities of up to 25 kg of ice condensed per hour. The stationary inner wall has a cold surface area of about 2 sq m. It is scraped by rotating blades of molybdenum alloy tool steel. An orthodox condenser without scraper would need to have a surface area of approx 100 sq m to achieve the same results, *i.e.* an ice crust not thicker than 0·2 mm. The ammonia refrigerator keeps the condenser walls and the ice receiver at −70° C. If the temperature were lowered further the hardness of the ice crust would increase so much that the bearings of the driving motor would suffer and the scraper blades would wear rapidly.

Consider the actual heat transfer and refrigeration requirements in, for example, the rotating scraper condenser model V55-D of the National Research Corporation. This has an effective surface of about 21 sq ft and condenses about 55 lb of ice per hour from water vapour at a pressure of approx 10^{-1} torr. If the ice crust thickness is kept at 0·3 to 0·4 mm by the scraper, the surface of the ice layer is at −45° F for a refrigerant temperature of −70° F. This temperature difference of 25° F is due to the combination of a difference of 12° F across the static film of the refrigerant (ammonia), 4° F across the wall of the steel casing, which is 14 mm thick, and 9° F across the ice crust. The refrigerating unit used is stated to provide '6 ton of refrigeration', *i.e.* 3312 frigoria hour.

Rotating scraper condensers of smaller sizes are rather less efficient: one for 25 lb of ice per hour needs 3 ton of refrigeration, one for 10 lb needs 1·5 ton, assuming in both cases an operating temperature of −70° F.

11.6. Freeze-drying

Much of the data in the preceding sections applies also to freeze-drying but there are further aspects of the sublimation in vacuum of water from the frozen state which need to be considered.

Vacuum drying at temperatures above 0° C has the advantage mentioned in § 11.2 over other drying procedures. Several further advantages result from freeze-drying which have proved to be particularly valuable in the dehydration of many chemicals and pharmaceutical products, serum, blood plasma, various antibiotics, hormones, vaccines, bone, cells, tissues and also foodstuffs. These advantages are (Flosdorf, F11):

(*i*) As the total pressure can be kept low if the material is at sufficiently low temperature (*see* Table 11.1) the final water content of the residue can be reduced to very small values. Furthermore, the oxygen content of the atmosphere at low pressure is so small that very readily oxidizable materials can be dried.

(*ii*) As the material is frozen, chemical changes are minimal so that labile substances can be dried; also, the material cannot bubble or froth, so surface changes which would be brought about by these phenomena are avoided. Moreover, bacteriological growth and changes due to enzyme action are halted. The chemical, biochemical, physiological and therapeutic properties of the products are therefore conserved.

(*iii*) The loss of certain essential volatile constituents (other than water) is small so that the vitamin content of foodstuffs like orange juice and (with certain precautions) the aroma in, for example, coffee is preserved.

(*iv*) Coagulation during drying is very unlikely, as the molecules are maintained in position in the frozen state. This is a great advantage in, for example, preventing the irreversible process known as 'denaturation' which is due to the aggregation of protein molecules.

(*v*) As the frozen solvent sublimes, the solute remains evenly distributed within the material and the dried residue is in the form of a very porous structure occupying essentially the same space as the original material. It is therefore readily soluble or reconstituted with conservation of the structure of the product.

(*vi*) As drying proceeds, the ice layer recedes gradually during the sublimation to leave the porous residue exposed without a hardened surface.

(*vii*) Storage properties of the freeze-dried product are excellent, *e.g.* dehydrated bacteria and viruses may remain unaffected for years.

Vacuum sublimation of water from the frozen state is akin to molecular distillation (§ 13.5). Every evaporating molecule should reach the surface of the refrigerated condenser (which is at a lower temperature than the evaporating source) without colliding with residual gas molecules in the evaporation space between the source and the target. Such collisions, as well as reflections of molecules at the walls and at the condenser surface, would produce molecular migration in the wrong direction and impair the efficiency of the process. As a rule-of-thumb method, to avoid collisions between the evaporated vapour molecules and gas molecules, the mean free path of the permanent residual gases in the vacuum should be greater than the distance between the evaporating source and the condenser surface. The cross-section of the path over this region should be as large as possible to avoid any major impedance to the flow of vapour molecules.

There are two stages in freeze-drying: first, ice is sublimed from the frozen material; second, moisture is removed from the final dried solid to a minimum level. Depending on the particular product concerned, 98 to 99% of the water is removed during the first stage. In the second stage, the residual moisture content is reduced to 0·5% or less of the final product by weight. In the first stage, the temperature is well below 0° C (32° F); as the change-over from the first to the second stage proceeds, the temperature rises and finally reaches room temperature.

There is an appreciable slowing down of the speed of evaporation of water vapour as the drying proceeds because this speed is limited by the maximum possible rate of diffusion of water vapour through the interstices of the porous, dry outer layers of the material, and this obstruction will increase as the ice recedes. However, the chief factor deciding the rate of removal of water vapour in freeze-drying is the difference between the vapour pressure of water at the surface of the material and that at the condenser surface. This is an optimum when the pressure at the condenser surface is about 55% of that at the surface of the material (Flosdorf, Hull and Mudd, FHM1). On account of other technical considerations, it may not be possible in practice to keep near this optimum.

Figure 11.6 is a plot of the vapour pressure differences obtained in the ideal case (*i.e.* assuming no restrictive orifices in the pipe line between the source material being dried and the condenser surface) for various condenser surface temperatures and temperatures of the source. The cross on each curve denotes the temperature of the surface of the ice on the condenser for which the slope of the curve is a maximum, giving rise to the maximum 'driving force' for transference of water vapour from the source to the condenser (Walker, Lewis, McAdam and Gilliland, WLMG1). These results apply only during the first stage of freeze-drying, *i.e.* when ice is being sublimed. As the fulfilment of these optimum conditions is unlikely, these results are of doubtful significance in practice.

It is manifest that the most favourable shape of a frozen product to be dried in vacuum is that of a thin layer. Either the material is frozen before it is loaded into the drying chamber or it is loaded directly into the chamber and **self-freezing** (auto-freezing) takes place because of the initial rapid loss of the latent heat on vaporization of the solvent (usually water). In the former case, the material is in small bottles (layer thickness not more than 1 cm) which are refrigerated and then placed in the drier or it is in the form of a layer a few millimetres thick in a flat dish or tray—a technique known as **shelf-freezing**. Alternatively, in the case of liquids, **shell-freezing** may be practised to provide the required thin layer. For example, blood plasma (§ 11.8) is subjected to shell-freezing by rotating the horizontal cylindrical containers on rollers in a bath of alcohol maintained at about −50° C (Fig. 11.7(*a*)); the plasma is then impelled under the centrifugal force acting against the inside wall of the container to form a thin shell provided that the container volume is at least twice the volume of the material. Shell-freezing may also be undertaken, but not at such low temperatures, by loading the material into bottles

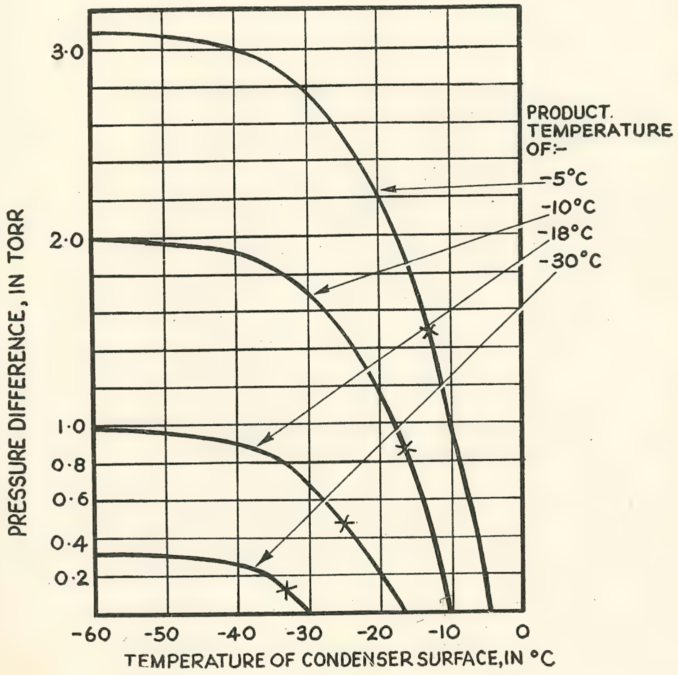


FIG. 11.6 Plot of the pressure difference against the condenser surface temperature for various temperatures of the surface of the material being dried

placed in racks in a vessel which is rotated and cooled by cold air circulation (Fig. 11.7(*b*)).

Materials which are pre-frozen by shelf- or shell-freezing are then placed in the drying chamber as a subsequent operation. In self-freezing, these two distinct operations are not necessary. However, foaming or frothing of the material due to outgassing during the initial stages of pumping is then a difficulty. Foaming could be reduced by restricting the rate of reduction of the pressure, but it is desirable that the freezing should be rapid. The centrifugal freeze-drying method (Greaves, G22) is a valuable solution of this difficulty for ampoule quantities of materials, as not only does it prevent foaming but also provides the desirable thin shell or wedge of the material against the ampoule walls. About 20% of the water evaporates before freezing occurs (Beckett, B34), but this is not harmful in many cases of the freeze-drying of blood plasma, vaccines, living bacteria, virus suspensions and antibiotics because the evaporation rate is sufficiently rapid to cause freezing within a few seconds. A typical centrifugal freeze-drier with a mechanically refrigerated condenser in the form of a 'cold coil' is shown in Fig. 11.8.

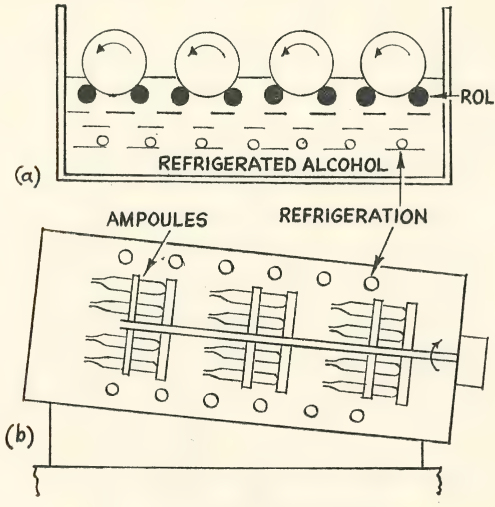


FIG. 11.7

(*a*) Shell-freezing in a bath of refrigerated alcohol
(*b*) Shell-freezing in a stream of cold air

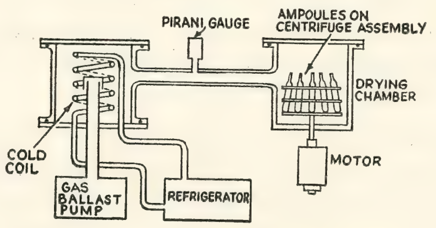
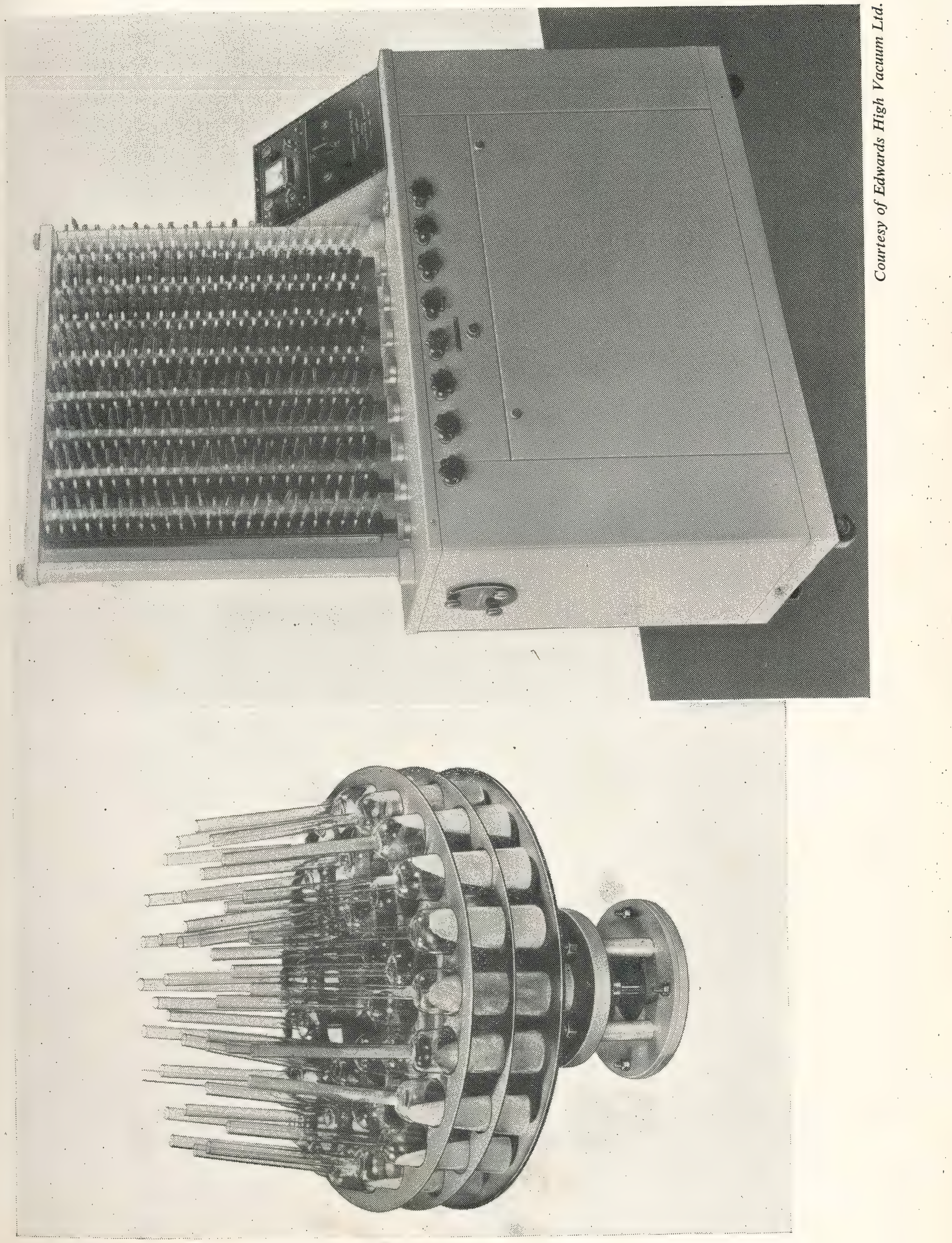


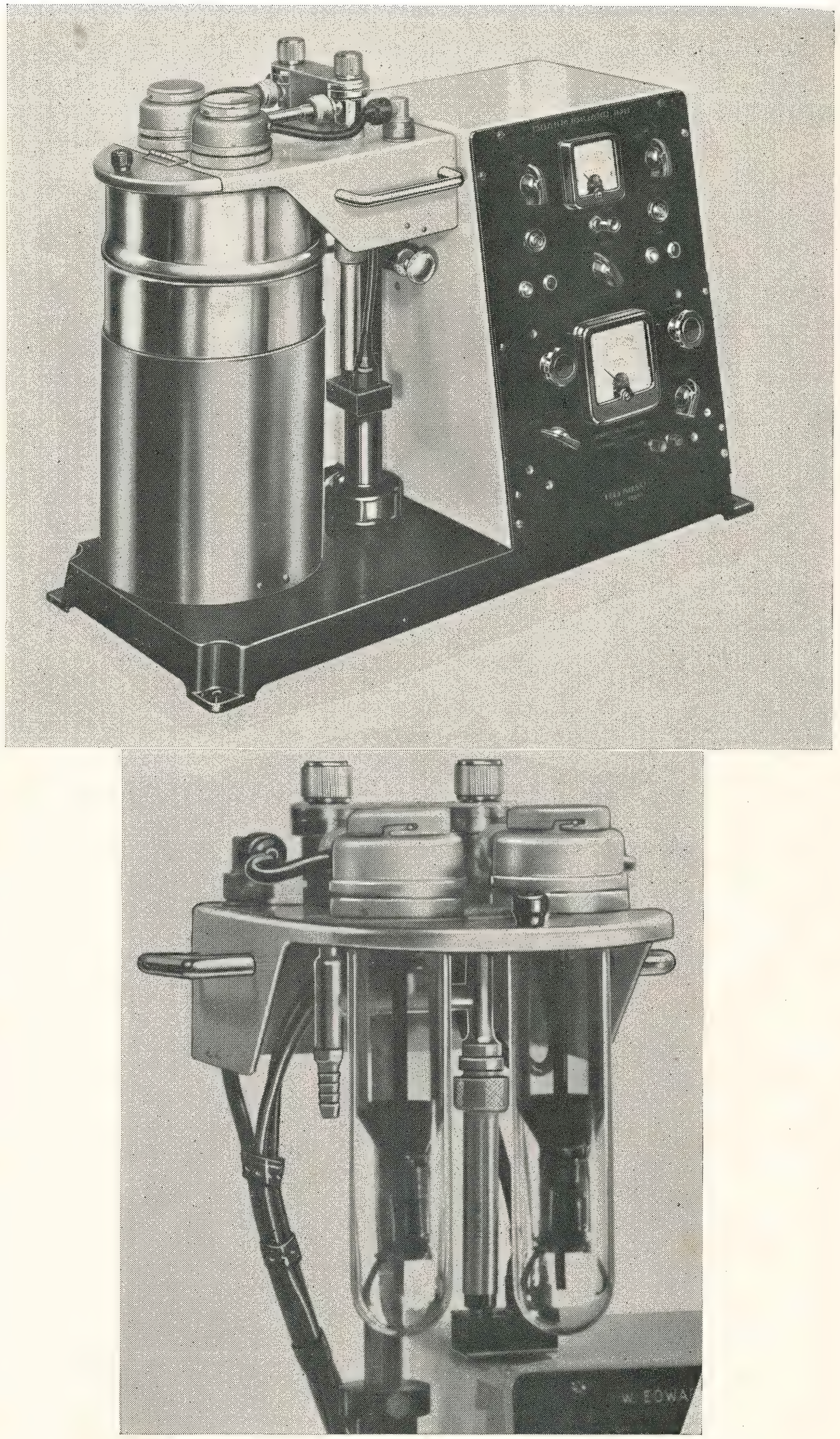
FIG. 11.8 Centrifugal freeze-drying



Courtesy of Edwards High Vacuum Ltd.

Plate 9

Left: centrifugal assembly of ampoules used in freeze-drier (an older type of arrangement which, however, shows the arrangement clearly and the wedge-shaped specimens in the ampoules). *Right:* secondary freeze-drying plant (*see* p. 421).



Courtesy of Edwards High Vacuum Ltd.

Plate 10

Top: a commercial tissue drier.
Bottom: drying head of the tissue drier (*see* p. 426).

Smaller plants utilize solid carbon dioxide plus methyl cellosolve for refrigeration or, instead of refrigeration, a chemical desiccant like phosphorus pentoxide. A centrifuge assembly of the ampoules containing the material is shown in Plate 9. Recently, Verma and Rowe (VR1) have shown that the breakage of these ampoules during freezing is minimized by coating the inside surfaces with water repellant 'Repelcote' (Hopkins and Williams Ltd.). Generally, two stages of drying are practised: primary drying in the centrifugal freeze drier until freezing is complete; secondary drying over long periods in which the ampoules are transferred to auxiliary headers (Plate 9) and the freeze-dried product within its ampoule is sealed-off by glass-blowing. Connection of the ampoule to the header of the secondary drier is either by rubber connectors or wax joints.

In freeze-drying, an important limitation to the speed of dehydration, which is often unavoidable, is the existence of 'bottle-necks' in the true sense of the word, as in the case of the shell-freezing and centrifugal methods. The medicine bottles and ampoules used, for example, in the dehydration of penicillin solutions and blood plasma are standardized in shape by the suppliers. The minimum cycle time tolerable has to be established, therefore, by preliminary dehydration experiments with single bottles, which are weighed continuously during these tests. During such trials a system with a large condensing surface is used so that this part of the equipment does not influence the results. Similar tests have to be carried out whenever plant for the dehydration of a new product is to be designed.

11.7. A Freeze-drying Plant for Batch Operation

A typical small plant is schematically illustrated by Fig. 11.9. The material to be dried is pre-frozen and placed in trays in the chamber 1. To achieve the low pressures required, a combination of a vapour pump backed by a gas-ballast rotary pump is used. The procedure is as follows:

(*a*) Close the isolation valves *A*, *B*, *C*, *D*, *E*, *F* and *G*.

(*b*) Start the two-stage gas-ballast pump 5 with the gas-ballast valve closed and check the pressure with a Pirani or thermocouple gauge to ascertain proper functioning.

(*c*) Open valves *A* and *C* and the gas-ballast valve to enable the pump 5 to remove moisture without contaminating the pump oil.

(*d*) As desiccation proceeds (the material looks 'moist' as distinct from 'wet' when its moisture content is of the order of 20%) and the pressure is less than 10^{-1} torr, close the gas-ballast valve.

(*e*) Close valves *A* and *C*, open valve *D* and start the vapour pump 4.

(*f*) Open valve *B* and dry the material to the required moisture content of a fraction of 1%.

(*g*) While this is done, remove the cooling mixture from the space 3 and warm the condenser slightly so that its wall temperature is raised a few degrees. The ice cone will then drop into the container 6.

(*h*) Open valve *E* and withdraw the container through the cover-plate 7.

A two-part cycle is described here, *i.e.* pumping firstly with the gas-ballast pump and, secondly, with the vapour pump also, to cover possible dehydration requirements down to 0·1% moisture. After such a pilot plant test it may be found possible with certain materials, not requiring such extreme drying, that the second part of the cycle can be omitted, *i.e.* the gas-ballast pump only is used in a simpler plant.

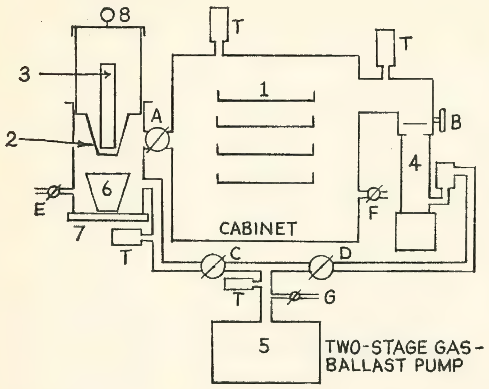


FIG. 11.9 Outline of freeze-drying plant for batch operation

1, Cabinet with trays; 2, ice condenser; 3, container for cooling mixture or space for cold coil; 4, oil diffusion pump; 5, gas-ballast pump; 6, receiver for ice cone from 2; 7, removable cover; 8, lid; T, thermocouple or Pirani gauge

Typical approximate figures indicate the possibilities in practice. The chamber 1 may have internal dimensions 2½ × 2½ × 2½ ft. The refrigerated condenser 2 may be designed according to Fig. 11.10 with a surface area of its cone of 2000 cm². An oil diffusion pump with an intake port dia of 4 in. to 6 in. and speed of up to 300 litre per sec at 5×10^{-3} torr is suitable with a gas-ballast rotary backing pump of displacement about 900 litre per min. In a 7-hour cycle about 3½ kg of ice might be deposited on condenser 2, yielding an ice cone about 1·75 cm thick. The surface of the condenser is maintained at −70° C by solid carbon dioxide plus methyl cellosolve; about 8½ kg of solid carbon dioxide is needed per kilogram of ice deposited on the condenser (allowing for about 25% loss through the insulation, which is mostly via the gasket seal of the condenser).

As an alternative to the use of solid carbon dioxide, a 'cold coil' condenser may be used which is maintained at a surface temperature of −70° C by a special refrigeration unit (G. and I. Weir Ltd.; Linde's Eismaschinen A.G.).

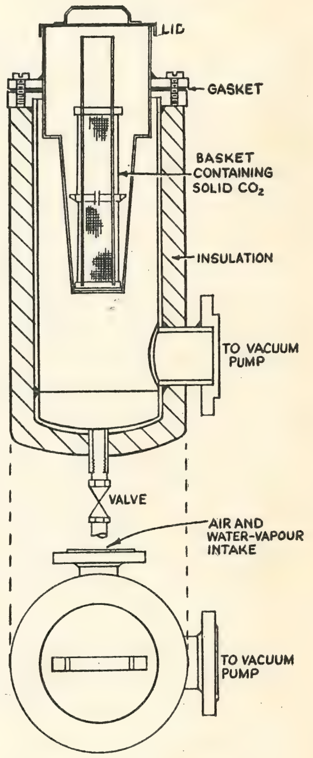


FIG. 11.10 Refrigerated condenser; refrigerant: solid carbon dioxide

This coil should be able to absorb about 3×10^4 cal per hour per 100 cm² of its surface, *i.e.* 6×10^5 cal per hour in the case in question.

The description of two freeze-drying runs using a laboratory plant of somewhat smaller dimensions than that just described give an idea of the process.

(*i*) 240 gram of solution containing 50 g of solid (a complex organic compound to be used for medical purposes) was prefrozen by mechanical refrigeration to −15° C. It was in two trays each about 440 cm² in area and the depth of the liquid was about 2·5 mm.

Figure 11.11 shows plots of the pressure, temperature and mass of this material against time during vacuum drying. The mass against time curve shows clearly three characteristic phases in the dehydration of a solution: (*a*) the constant rate of removal of water over a period of about 2 hours; (*b*) the subsequent period of about 2½ hours during which this rate of removal falls off; (*c*) the slow removal of moisture during the final desiccation period. These three phases are also reflected in the pressure against time curve. During the first phase, the temperature falls rapidly from −15° C to −38° C. This fall is due to rapid evaporation of the water vapour and the consequent loss of latent heat of vaporization by the solution; this fall was not compensated by supplying heat to the material.

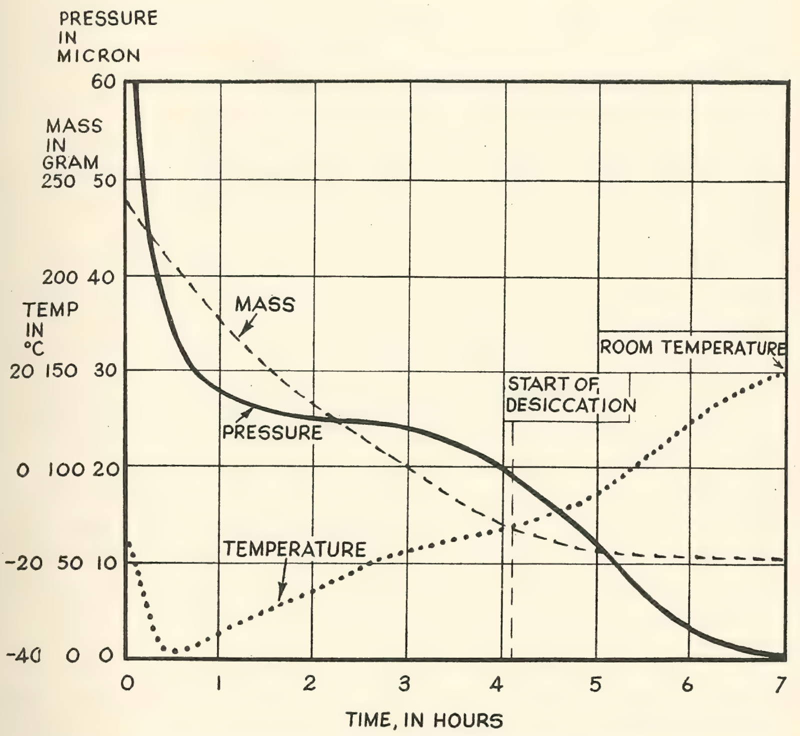


FIG. 11.11 Plots of pressure, temperature and mass of material against time during freeze-drying

The speed of evaporation during the first $4\frac{1}{4}$ hours (when about 184 of the 190 gram of water were evaporated) was about $1{\cdot}3 \times 10^{-2}$ mg per cm² per sec at an average temperature of about −20° C and with a refrigerated condenser surface temperature of about −70° C. This condenser had a total surface area of 910 cm² so that, after the run, it was covered with an ice crust about 2 mm thick. The end product was 50 gram of solid in the form of a very light powder which was instantly soluble in water (without agitation). The parallel product, dried at atmospheric pressure at room temperature, took several minutes to dissolve with violent agitation.

(*ii*) In the same plant, 40 cc of a 25% solution of sodium chloride was dried in a single tray at about −30° C. The rate of water evaporation was 9×10^{-3} mg per cm² per sec. The end product was in the form of very small crystals of uniform particle dimensions of about one micron.

It must be emphasized that only approximate figures are available for the speeds of evaporation quoted. Moreover, despite the importance of these figures in deciding the dehydration schedule times, they cannot be obtained by other than experimental trial. Owing to the complicated 'geometrical' conditions under which the evaporation of water from a frozen cake takes place, neither the true area nor the true temperature of the evaporating source can be assessed correctly. Further, evaporation does not take place freely into a vacuum as theory has to assume (Adam, A15; Dushman, D1). Thus, the practical figures for the speeds of evaporation are very different from those one would derive from theory on the basis of the vapour pressure of water as a function of temperature. In fact, the practical figures are only about 1/1000 of the calculatable ones.

Obviously the exact value of the rate of evaporation in mg/cm²/sec under the same temperature conditions will vary according to the nature of the product which is freeze-dried. The order of magnitude of this figure will not, however, vary significantly from one material to another and from one freeze-drying equipment to another (Flosdorf, F10; Bradish, Brain and McFarlane, BBM1).

Neumann (N11) describes a convenient apparatus in which the mass of the product is determined by means of a Rayleigh current balance within the vacuum chamber during freeze-drying.

11.8. The Freeze-drying of Blood Plasma

An example of a larger scale freeze-drying operation in which pre-freezing is undertaken is the processing of blood plasma. The Stokes Corporation outline the procedure necessary before the freeze-drying is begun; briefly this is as follows: bottles contain 1 pint of blood with the appropriate amount of anti-coagulant; the filled bottles are centrifuged at 1800 r.p.m. in a horizontal position to separate the plasma and the heavier red blood cells; the plasma is transferred by vacuum suction from the bottles through sterile tubing to sterile stainless steel containers; the plasma is clarified by further centrifuging at 7200 r.p.m.; the clarified product is fed under air pressure to a trough above which rotates a stainless steel cylinder just touching the plasma surface; the thin layer of plasma picked up by the cylinder is irradiated with ultraviolet light to destroy any contaminating micro-organisms; a scraper against the rotor transfers the plasma into a collecting pan; the plasma is transferred by positive sterile air pressure to the final bottles; biochemical tests are carried out; a special synthetic rubber sealing cap is put on the bottles; the plasma in the bottles is *shell-frozen* by rotating the bottles mechanically in the surface of a bath of alcohol at −50° to −70° C (Fig. 11.7); the bottles containing the plasma are then stored in a refrigerator at −20° C.

When the freeze-drying is undertaken, the bottles of frozen plasma are pre-cooled to −40° C and their sealing caps half released to permit air and moisture to escape before they are placed on shelves in the freeze-drying chamber. These shelves are maintained initially at about 5° C by the circulation through pipes of chilled water. The gas-ballast pumps are operated to produce gradually a pressure of 5×10^{-3} to 10^{-2} torr, and a refrigerated condenser at −50° C (two-stage ammonia refrigeration) is used to collect the sublimed water vapour. During this sublimation the product remains frozen even over very long periods, a cycle of several days being involved. The condenser ice is removed between batch operations by the application of steam, or continuously during the drying by a rotary scraper in the National Research Corporation plant. After removal of the bottles of dried plasma from the drying chambers, final stoppers are placed loosely in position and the bottles are evacuated on auxiliary plant to a pressure of about 20 to 30 torr which also ensures that the stoppers are pressed firmly in position. The freeze-dried plasma stored in vacuum has a shelf life of several years.

Plants for the freeze-drying of blood plasma and of penicillin have become large installations in recent years and tend to utilize extended refrigerator surfaces.

11.9. The Freeze-drying of Surgical Grafts and Tissues

Further recent developments in freeze-drying in the medical field are concerned with products which are so sensitive to chemical and/or biological action that low temperatures of −60° C or −70° C are demanded. An example is the extraordinary new process of providing dehydrated bones, skin for grafting and even arteries obtained from fresh human corpses (graphically described by Americans as 'fresh cadaver material'). On reconstitution after storage in the 'tissue bank' (*see* Eastcott, E8) the 'spare parts' are available for surgical operations.

Eastcott (E8) has described a simple plant for the freeze-drying of arteries used in experimental work at St. Mary's Hospital, London. The artery (*e.g.* aorta or femoral) is inserted in a sterile Pyrex tube with a rubber cap and immersed in a mixture of solid carbon dioxide and alcohol (−78° C max) to be frozen to about −60° C in about 15 min. It is then transferred to the artery bank where it is kept in air at −70° C or lower. The drying is then in two stages. In the first the deep-frozen artery in its glass tube (with cap replaced by a sterile gauze bacterial filter) is placed in a simple vacuum plant (Fig. 11.12) consisting of the glass drying chamber (uncooled) beneath a cold-trap filled with solid carbon dioxide and alcohol with pumping only by a small two-stage mechanical rotary pump. This provides an efficient short wide path from the product to the condenser surface. Pressure monitoring is by two Pirani gauge heads, one at the drying tube and the other at the pump; the pressure decreases to about 3×10^{-2} torr at the end of this primary drying, which takes 6 to 10 hours. The moisture content is then about 5%. The secondary drying to about 2% moisture content is simply in an evacuated desiccator containing trays of phosphorus pentoxide; this requires a period of at least 3 days. On removal from this vacuum desiccator the sterile gauze filter is replaced by a special cap through which the tube is evacuated via a hypodermic needle; the final sealing is by Apiezon wax.

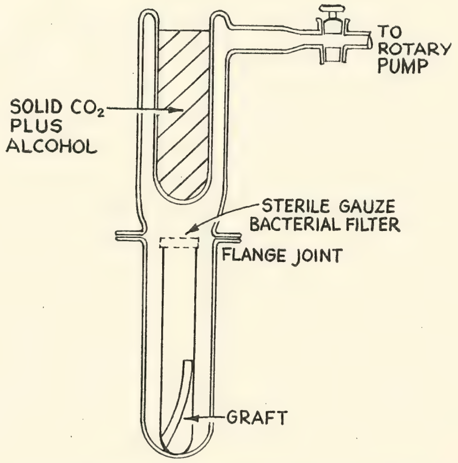


Fig. 11.12 Primary freeze-drying of arterial grafts (*after Eastcott*)

A plant for freeze-drying artery grafts is also described by Gardner and Leemans (GL1). To avoid the risks of bacterial contamination associated with two-stage drying, the process is carried out in a single tube; the vacuum plant is arranged for freeze-drying, desiccation *in vacuo* over phosphorus pentoxide, storage and final reconstitution.

Naidoo and Pratt (NP1) describe an experimental plant for freeze-drying brain enzymes to preserve their histological properties and retain high enzyme activity.

A commercial tissue drier (Edwards High Vacuum Ltd., Model TD2) is shown in Plate 10. The specimen is pre-frozen by immersion in isopentane cooled by liquid nitrogen or Freon 12 cooled by liquid air. It is then transferred on its carrier to inside the drying head (Fig. 11.13). This consists of a glass tube with a demountable vacuum-sealed metal top and a quick-acting metal lid which is sealed by an O-ring. Two 10 mm dia specimen carriers, one above the other, are suspended from the lid. Surrounding the specimen carriers within the drying tube is a thermostatically controlled heater. The drying tube is immersed in a Dewar flask containing solid carbon dioxide and alcohol. By adjustment of the thermostat, the specimens can be maintained at a recorded temperature between −50° C and −10° C. Evacuation is by a two-stage mechanical rotary pump with a phosphorus pentoxide trap. Water vapour which sublimes from the frozen tissue is mostly condensed on the walls of the drying tube; the remainder is absorbed by the desiccant trap. At the end of the drying, the head is brought up to room temperature; the condensed ice on the walls then sublimes, but is absorbed in the phosphorus pentoxide trap and does not return to the specimen.

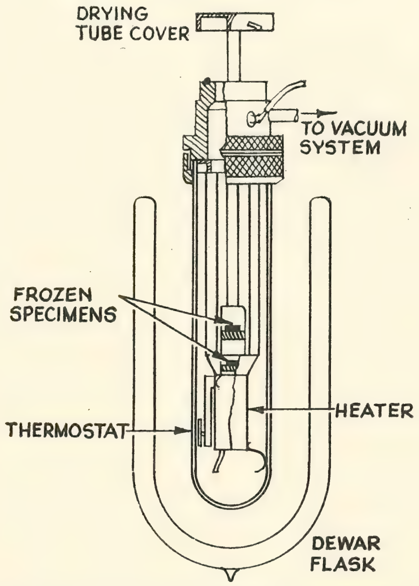


Fig. 11.13 Drying head for Edwards TD2 tissue drier

11.10. Further Applications of Vacuum Drying

In this necessarily brief survey of a somewhat complicated technique in vacuum engineering, an idea only of the problems involved and some suitable ways of solving them have been sketched. A great variety of special applications of vacuum-drying and of freeze-drying may be encountered in addition to those discussed. Typical problems put to the manufacturers of vacuum equipment include the dehydration of peat (which contains 90% water), dog food, grass (without loss of vitamins and chlorophyll), protein solutions for the production of whipped cream and drugs. Though the basic principles of vacuum technique concerned are the same in all cases, the details of plant and its shape and size will vary considerably, not to mention economic considerations.

An incomplete list of substances which have been freeze-dried, and must be freeze-dried because there is no other way to prepare them, includes:

Albuminous substances: milk powder from human milk; fibrin; prothrombin; haemoglobin; brain tissues; many types of sera.

Plasma substances: blood for blood transfusions.

Drugs and medicine: tuberculin preparations; cholesterol preparations; vitamins for injection purposes.

Antibiotics: penicillin compounds and preparations of streptomycin.

Bacteria and virus cultures.

Vaccines, *e.g.* for contagious diseases; against encephalitis; pig cholera virus vaccine (Flosdorf, F10).

Cells and tissues, especially for the conservation of living cells.

Gelatine foam for brain operations.

Materials for which vacuum-drying has been (but is not necessarily) used include the drying of precipitates which have been pre-dried by centrifuging, the dehydration of polyamide fibres to less than 0·1% moisture content, the drying of paper, paper capacitors, cables, transformer oils (*see* Chapter 12) and of textile fibres before spinning.

For further details see the books by Flosdorf (F10), Neumann (N10) and 'Freezing and Drying' (Symposium reports 1951 and 1959, Institute of Biology, London).

12

VACUUM IMPREGNATION

12.1. Principles Involved and Examples

In practice the process of vacuum impregnation involves two chambers; in one of these (the vacuum tank) is placed the material to be impregnated and in the other (the impregnant storage tank) the liquid impregnant. These chambers are connected by a duct containing a valve. With this valve closed, the vacuum tank containing the material is pumped to remove air and moisture; in some cases, heating is also applied. The valve is then opened so that the impregnant flows into the base of the vacuum tank and rises to cover the material. The valve is closed again and air at atmospheric pressure (or above in some cases) admitted to the vacuum tank. The liquid impregnant is thereby forced into the pores of the material. After standing for a time, ranging from minutes to hours depending on the material concerned, the impregnant is drained back into its original tank by the application of positive pressure, and the impregnated material is removed, dried and, sometimes, baked.

Impregnation is undertaken in the processing of porous materials in order to achieve one or other of the following results:

(*i*) Filling of the empty pores of the material.
(*ii*) Replacement of the substance in the pores by another.
(*iii*) Conditioning of the surface of the pores in a required manner.
(*iv*) Blocking of the interconnections between pores.

The common requirement of all processing methods for both the materials to be impregnated and the materials to be used as impregnants is the removal of moisture and/or unwanted volatiles. These are present in varying—and sometimes in minute—quantities. Moisture may adhere to the outer and/or 'inner' surface of a solid and part of it may be chemically bonded to the solid. For example, paper can be dried without damage to its mechanical properties, but if the chemically bonded or 'structural' moisture is removed by heating to 120° C, it becomes brittle. Impregnants may contain moisture suspended in small bubbles or may have a certain solubility for water. In all cases where the moisture is adsorbed, the thin film of water has physical properties different from those of ordinary water; in particular, the vapour pressure at a given temperature is lower and it is consequently more difficult to evaporate.

Examples of the four cases given above are:

(i) (*a*) Cast metal parts, intended for use in vacuum systems, sometimes show air-leaks through inter-connected pores. These may be filled by impregnation with a heated resin which solidifies at the temperature at which the casting is used. Tin may also be used as an impregnant.

(*b*) The resistance to mechanical or thermal shock of sintered ceramic parts may be substantially increased by impregnation with a plastic resin.

(*c*) The paper, to be employed as a dielectric for capacitors and electric cables, has to be impregnated with a highly insulating oil or wax in order to increase its breakdown voltage. Air must be excluded from the pores.

(ii) (*a*) The water absorption of porous materials, *e.g.* textile fibres as used for electric insulation, is materially decreased by first driving the water out and then impregnating with a water-repellant plastic.

(*b*) The combustibility of certain kinds of cardboard used in building may be decreased by impregnation with an incombustible filler.

(*c*) Drying and impregnation is used for the preservation of wood.

(iii) (*a*) The conditioning of the surfaces of pores, without filling them, is an important technique. It is used in sterilization, *i.e.* protection against living organisms, like spores, fungi and bacteria.

(*b*) To enhance chemical reactions between gases, a catalyst may be deposited in the pores of a solid, which is in contact with these gases.

(*c*) When a substance is to be used in the porous state it can be protected against chemical attack by coating its outer and 'inner' surfaces.

(iv) Blocking the inter-connection between the bubbles or cavities in a porous body (the walls of the pores being impermeable) by an elastic resin or other material which forms a film, one may produce a material of low specific bulk density, *e.g.* a light building brick or a float may be treated in its final form. In most cases the impregnation needs only to be carried out to a depth of a few millimetres from the external surface.

12.2. Pre-treatment before Impregnation

As a rule, the material to be impregnated and the impregnant have to be dried and degassed in the first stages of the process. Economic considerations permitting, the engineer will choose vacuum pre-treatment (combined with heating) as the best way to remove gases and vapours. Table 12.1 summarizes a few of the processes in which vacuum practice has been used (Holland-Merten, H5).

For each of the processes given in Table 12.1, the vacuum engineer has to find out the minimum requirements to solve the individual problem. For example, in the impregnation of wooden railway sleepers, the vacuum requirements can be met by the use of single-stage gas-ballast pumps provided with water-cooled surface condensers on the intake side (§ 11.4). The pumping capacity required can be calculated from pilot plant experiments on small samples. On the other hand, for the impregnation of high voltage paper capacitors, the drying has to be continued until moisture residues of only a few thousandths of one per cent are encountered in both the capacitor dielectric and the impregnant. The vacuum equipment used must therefore be capable of producing pressures of the order of 10^{-4} torr and may use Roots pumps or oil ejector pumps backed by gas-ballast pumps. Such requirements cannot be guessed or deduced analytically from first principles; experience is essential: the degree of drying must be checked against experiments on dielectric breakdown or other electrical characteristics of the finished product and the results analysed statistically.

TABLE 12.1

Some processes in which vacuum treatment has been used for the removal of moisture and sorbed gases before impregnation

Sterilization and disinfection by formalin vapour, steam, etc., of surgical dressings, fruits and other foodstuffs, ampoules, tobacco seeds

Surface treatment in the deposition of catalysts on surfaces of pores, chlorination, staining of wood and the mercerization of cotton

Treatment in bulk for

(*a*) *Preservation*; *e.g.* wood of telegraph poles, railway sleepers, carpets, furs, cloth

(*b*) *Decreasing combustibility*: wood, paper, textiles

(*c*) *Increasing density*: ceramic materials

(*d*) *Decreasing water absorption*: textiles, paper

(*e*) *Increasing strength*: wooden shuttles; wood for pencil making, tool handles, tennis rackets, etc.

(*f*) *Improvement of dielectric properties*: insulation on electric motor windings; high voltage capacitors; electric cable insulation

A suggested method of gaining such experience without too great an expenditure of time and money is to suspend a test piece (*e.g.* one, or a few, capacitors) on a balance in the vacuum chamber. The balance could be a spring balance (a lever type spring balance would record to 0·2 gram in 100) or a torsion balance or a Rayleigh type current balance (*cf.* Neumann, N11). The chamber would need to be large compared with the test piece and equipped with high speed pumps. The change of mass of the article on dehydration *in vacuo* with various heat treatments would then be measured. The results would give the minimum time required for the water to escape by permeation through the material of the sample depending on its structure and also furnish data as to the quantity of water vapour and other volatiles to be disposed of at different times in the cycle. This information would assist in the choice of pump, cooled condenser and receiver required in the production plant. The test method for amounts of moisture less than 0·5% would preferably consist of the measurement of some particularly moisture-sensitive property of the sample, *e.g.* in the case of paper capacitors or cable, the power factor at high frequency.

What has been stated about the drying and degassing of the materials to be impregnated also applies to the impregnants. Extensive experimental investigations have been carried out recently on the gas content and water absorption of high boiling liquids at pressures in the range from 1 to 10^{-2} torr by Oetjen and Gross (OG1).

Of the many applications of vacuum impregnation three processes are considered in the following text: the impregnation of castings (§ 12.3) which is representative of practice in which only a rough vacuum is required; the impregnation of paper capacitors (§ 12.4) and of electric cables (§ 12.5), in both of which a medium high vacuum is required.

12.3. The Impregnation of Castings

The sealing of porous castings is an important process in industry generally and in the provision of vacuum chambers, large vacuum pump bodies and other components in vacuum technology in particular.

Hull (H26) emphasizes that a satisfactory impregnant should have low viscosity, low volatility, should dry with small loss of volume, should withstand heating to 150° C and not have a deleterious influence on machinability. Styrene with linseed oil or dehydrated castor oil are recommended.

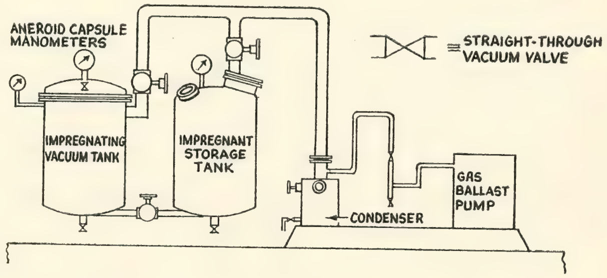


FIG. 12.1 Vacuum impregnation plant

The castings are first washed and degreased in detergent, rinsed, and dried for about an hour at about 130° C. After cooling they are transferred to the vacuum tank in which a vacuum of about 20 torr is produced by mechanical rotary pumps. The impregnant is then admitted by opening the valve connection to the impregnant storage tank. After soaking for a time depending on the size, type and material of the casting, with the vacuum pump still operating, the pumps are isolated and air is admitted to the vacuum tank (the valve being closed) at a positive pressure of 60 to 100 lb/sq in. After a suitable soaking time (20 to 60 min) the valve is opened so that the impregnant liquid flows back into its storage tank, the castings are removed, washed with thinners and then heated in an oven for curing. To arrive at the appropriate temperatures and times in the processing, pilot experiments on small samples are necessary before embarking on large-scale operations.

Several firms manufacture apparatus for vacuum impregnation (*see* Appendix D). The Pulsometer Engineering Company recommend a phenol-formaldehyde bakelite solution as an impregnant for castings of steel, cast-iron, aluminium, gun-metal and bronze. For aluminium-magnesium castings the Stokes Corporation use sodium silicate as the impregnant. The vacuum tank is evacuated to a pressure of 1 torr or less by rotary pumps protected by a condenser and maintained at this pressure for about an hour for each $\frac{1}{4}$ in. depth of penetration required of the impregnant. Final curing is for 2 hours at 100° C and at 150° C for the third hour. The apparatus used is shown in Fig. 12.1.

12.4. The Impregnation of High Voltage Paper Capacitors

The following description of practice adopted in the German industry for the impregnation of capacitors with trichlorodiphenyl ('Clophen', 3Cl) gives an idea of the problems involved and the methods of solving them. A high voltage capacitor, characterized by the fact that its insulation has a breakdown field strength of about 14 kV/mm, consists of two metal foils, which are insulated from each other by impregnated paper. This combination is wound into a flat spiral and compressed to form a solid block. To minimize the risk of puncture, the paper insulation consists usually of three layers, each 5 to 6 micron in thickness. Experience has shown that certain types of paper are suitable, and that they have to be impregnated with a liquid which has a dielectric constant and specific breakdown voltage higher than that of the paper. Trichlorodiphenyl is a suitable liquid. The impregnation is only satisfactory if the paper and the 'oil' are both free of moisture and gas.

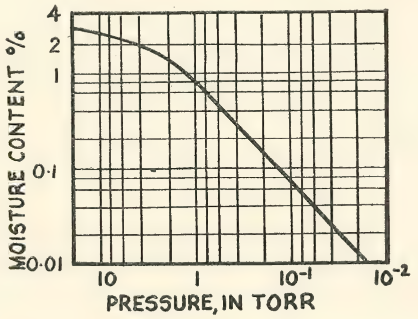


FIG. 12.2 The dependence of the moisture content of paper on the water vapour pressure at 40° C

At first sight, the apparent procedure would be to heat the capacitor and the impregnant to, say, 150° C to evaporate the water and then carry away the steam produced by hot air. But this cannot be done, because paper becomes brittle at about 120° C and, to be safe, it is necessary to keep below this temperature by at least 20° C. The only safe way to remove the moisture and air at lower temperatures is to use vacuum.

Fig. 12.2 shows the relationship between residual moisture (per cent of weight of paper) and the water vapour pressure surrounding the paper at 40° C (E. Leybold's Nachfolger). Above 2 torr, the vapour pressure is seen to have only a slight influence, namely, a change from 3% at 20 torr to 1·5% at 2 torr, but if the water vapour pressure is lowered to 10^{-1} torr, the moisture content falls to 0·06%, whilst if it is decreased to 10^{-2} torr, then the moisture content is as low as about 0·001%. The pumping system will, therefore, have to reduce the residual air pressure in the vacuum tank to, at most, 10^{-3} torr and, preferably, to 10^{-4} torr in order to provide a safety factor of at least one order of magnitude.

Apart from these requirements of the pumps and air-tightness of the vacuum tank, appreciable quantities of water, of the order of 3% of the weight of the paper in the capacitor, have to be removed. This means the use of pumps of which the performances are not affected adversely by water vapour. Gas-ballast pumps (§ 2.5) in conjunction with water-cooled surface condensers (§ 11.4) of minimum possible impedance to gas flow are recommended. For pressures between 1 torr and 10^{-2} torr, oil vapour ejector pumps (§ 2.18) are not disturbed by water vapour and organic vapours (which cannot be tolerated with gas-ballast pumps) especially if they are also provided with condensers and receivers for water disposal. Condensers and receivers should also be used on the discharge side of gas-ballast pumps to prevent water from condensing in the outlet tube and then flowing back into the pump, leading to contamination of the oil.

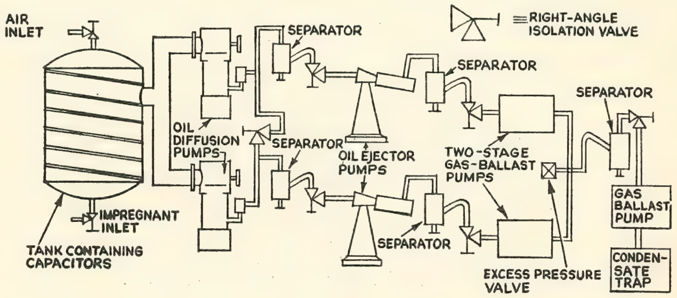


FIG. 12.3 Degassing, drying and impregnation of high voltage capacitors (A separator consists of a water-cooled surface condenser and a receiver which is emptied periodically)

A typical plant for the degassing, desiccation and then impregnation of paper capacitors is illustrated schematically by Fig. 12.3 (Jaeckel and Nöller, JN1). The impregnation tank, which may have a capacity of 10 to 25 cu m, is provided with heaters, indicated by the spiral lines around the tank. Oil diffusion pumps working at pressures below 10^{-2} torr are used. These are backed by oil-ejector pumping working at 10^{-2} to 1 torr which, in turn, are backed by two-stage rotary gas-ballast pumps working in the range from 1 to 10 torr. The final backing stage is a single-stage gas-ballast pump working between 10 torr and atmospheric pressure. For a 10 cu m tank, a single diffusion pump of a speed of about 6000 litre per sec is necessary, but two in parallel are required for a 25 cu m container. For such a single diffusion pump, the backing ejector pump would need to have a speed of about 60 litre per sec and the gas-ballast pumps a displacement of some 40 litre per sec.

The cycle time for such plant is not decided by the speed of evacuation of air and vapour from the tank but by the speed of effusion of the gases and vapours out from the very narrow slits between the paper and metal foils of the capacitor.

Fig. 12.4 shows the pressure against time graph of the pumping cycle for a 25 cu m tank charged with capacitors (Jaeckel and Nöller, JN1).

For the degassing and drying of the impregnant, *e.g.*, 400 kg per day is a typical consumption, a separate vacuum system is used and the purified product kept in an evacuated storage tank. The 'oil' as received has a moisture content of 0·1 to 1%. It is filtered, pre-heated and pumped by vacuum-tight toothed wheel delivery pumps (commercial models for liquids, but modified to make them suitable for vacuum) into a heated degassing tank in which an air pressure of a few torr is maintained by two gas-ballast pumps in series. To get rid of the bulk of the moisture in the filtering the liquid runs through an annular cylindrical space formed by two concentric cylinders of different diameters and provided with small holes in their walls, the cylindrical space being filled with a packing of bodies having large surface area but small bulk (Morton, M19; Rumford, R21), *e.g.* 'Raschig rings'. The liquid is thus spread in a thin film over a large surface so that small bubbles which might be distributed in it are set free. From this tank the liquid is pumped by a second similar vacuum-tight delivery pump into a second tank which is heated and pumped by an oil-ejector pump with gas-ballast backing pumps to a pressure of about 10^{-1} torr. The liquid is then passed into a third tank which is maintained at about 10^{-3} torr by an oil diffusion pump backed by an oil ejector and gas-ballast pumps. Experiment shows that this processing guarantees a moisture content of less than 10^{-4} gram per kilogram of a typical insulating oil. During the processing the oil loses some of its volatiles, which have to be collected and separated before they reach the gas-ballast pumps in order to prevent contamination of their oil.

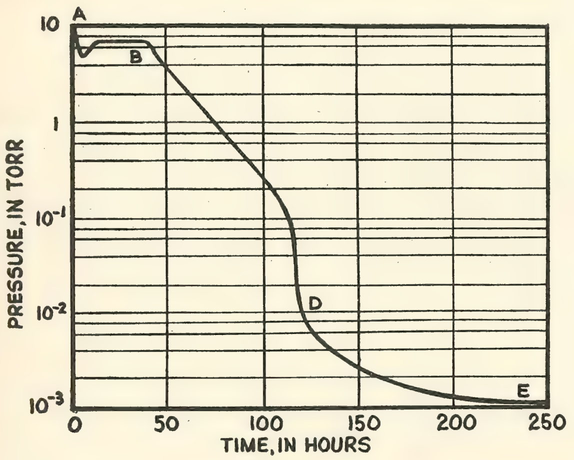


FIG. 12.4 Pressure against time curve for impregnation plant

A–B Working range of gas-ballast pumps
B–D Working range of oil-ejector pump
D–E Working range of oil-diffusion pump

The dehydrated and degassed liquid is finally pumped into a storage tank by a vacuum-tight delivery pump. This tank is kept at a pressure of 10^{-3} torr by a separate pumping system, consisting of an oil diffusion pump and a mechanical rotary backing pump, which needs no special protection against moisture.

The storage tank delivers the clean impregnant into the impregnating tank under high vacuum. Thus no bubbling occurs, and the impregnant is very easily and quickly absorbed by the porous material. No additional pressure is used, because the attraction into the pores for the impregnant provided by capillary forces forms a very much more efficient process than any high external pressure could furnish. The surplus oil is pumped back under vacuum into the storage tank before the vacuum in the impregnation tank is broken, so that the impregnated articles can be withdrawn.

12.5. The Impregnation of High Voltage Electric Cables

The problem here is similar to that discussed in the previous section. However, new difficulties are introduced because the paper insulation between the conductors is much thicker (of the order of 1 cm) so that the moisture, which amounts to 3 to 7%, has to traverse a long path to reach the vacuum. Moreover, at 40 kV/cm, which is the accepted upper limit for cable insulation testing, the breakdown danger due to ionization of traces of gases or vapours in the pores is great.

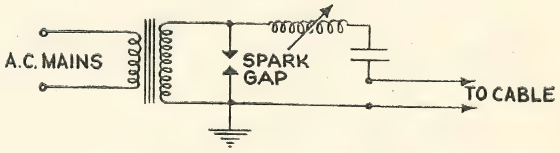


FIG. 12.5 Use of damped, oscillatory currents in heating uniformly a cable

In the past, attempts have been made to heat the cable core by electric current, or heat the tank, to enhance the escape of gases and moisture *in vacuo*. This is, however, a very slow process because of the low thermal conductivity of paper, and, moreover, uniform heating over the whole cross-section is essential, without over-heating leading to brittleness of the paper.

Of recent years, radio-frequency dielectric heating of the paper insulation has been employed. Here the conducting cable core and sheath are used as electrodes. At first, this method was also disappointing, because standing waves formed on any considerable length of cable, leading to over-heating of some parts of the insulation and under-heating of others. A very simple way out of this dilemma has now been found successful: it is to use damped oscillations instead of continuous ones. An r.f. generator of frequency about 500 kc/sec consists of a tuned circuit containing a spark-gap, which has a stream of compressed air played upon it (Marx, M20). One of the cable conductors is connected to one plate of the capacitor of the tuned circuit and the other to the earthed side of the spark-gap (Fig. 12.5).

The effect of this arrangement—which was applied to cable impregnation by K. Brinkmann at the Technische Hochschule, Braunschweig, in co-operation with E. Marderwald of the Osnabrücker Kupfer und Drahtwerk (Brinkmann and Marderwald, BM1)—is to provide a perfectly even energy distribution throughout the cross-section and length of the cable so that the degassing can be carried out at temperatures of about 75° C, *i.e.* well below the danger point (120° C). The method is also much quicker and hence more economic than previous heating procedures tried.

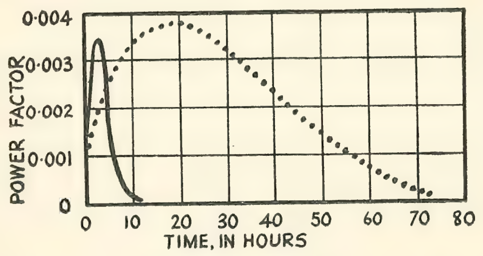


FIG. 12.6 Power factor against pumping time for a 30 kV paper insulated cable of length 5500 m. Full curve: dielectric heating used. Dotted curve: tank is heated (*after E. Leybold's Nachfolger*)

Figure 12.6 shows clearly the difference in the times for degassing and drying *in vacuo* depending on whether the vacuum tank containing the cable is heated (dotted curve) or dielectric heating with damped oscillatory currents is used (full curve). Here the degree of desiccation is indicated by the power factor. This factor increases to a maximum of 0·0035 after about 3 hours and then falls sharply to about 0·0001 after 10 hours if dielectric heating is used.

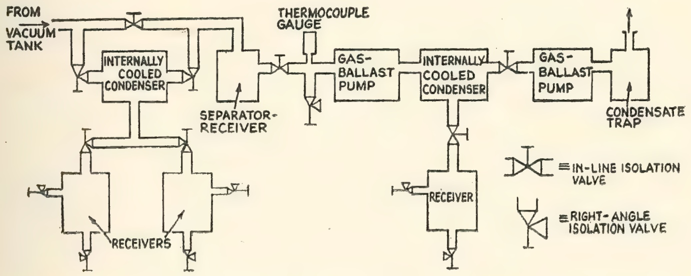


FIG. 12.7 Vacuum-drying of cable

If the tank itself is heated instead, this low dielectric loss is not attained even after 70 hours; moreover, it is necessary to heat the cable in the evacuated tank to 120° C.

Figure 12.7 shows an outline of the arrangement of the pumps, valves and internally cooled condensers for cable drying in which cables incorporating two tons of paper insulation are to be impregnated (E. Leybold's Nachfolger). The main condenser has a condensing surface area of 6·5 sq m (about 8 sq yd) whilst the subsidiary condenser surface area is 1 sq m. The gas-ballast pump used has a free air displacement of 600 cu m per hour; it is backed by a second gas-ballast pump of displacement about 50 cu m per hour; the second pump only is operated with air ballast. The receivers for condensed water are emptied periodically whilst the separator receivers, at the inlet and discharge of the gas-ballast pump combination, are for the collection of water condensing in the ducts.

Plate 11 shows plant for the vacuum impregnation of high-voltage measuring transformers.

13

DISTILLATION AND MOLECULAR DISTILLATION*

13.1. Principles of Distillation

Distillation is a unit operation used for the separation of the constituents of mixtures of liquids by partial vaporization and subsequent condensation. It is based on the fact that the vapour is relatively richer in the component whose addition to the liquid mixture would result in an increase of total vapour pressure (Konowaloff's rule). In general, therefore, the vapour obtained by boiling a mixture of liquids differs in composition from the original liquid as it is richer in the more volatile components. The completeness of separation depends on certain properties of the substances distilled, the type of equipment used and the chosen operating conditions.

Distillation may be carried out either as **simple distillation** or **fractional distillation (rectification)**. In simple distillation the liquid in the still is partially vaporized and the vapours recovered by condensation. The process is thus similar to evaporation, the difference being that in distillation the condensate is recovered whereas in evaporation, usually concerned with water, the condensate is discarded.

Simple distillation is characterized by the following steps:

(1) Transfer of heat to the liquid in the still in order to provide the latent heat of vaporization and maintain the liquid at the boiling temperature.

(2) The formation of vapour.

(3) The movement of vapour from the vapour liquid interface to the condensing surface.

(4) The condensation of vapour on the condensing surface which is kept at a comparatively low temperature.

By successively condensing the vapour and boiling off a portion of the condensate a further increase in the concentration of the more volatile component can be obtained. In rectification all these successive vaporizations and condensations are carried out simultaneously and a part of the condensed liquid, called the **reflux**, is returned to the column in countercurrent to the flow of vapour. This results in an increased separation without an additional heat input since the partial condensation of the less volatile components provides the latent heat necessary for the partial evaporation of the more volatile components. Hence, the basic requirement in the design of a rectification column is to bring the rising stream of vapour into intimate contact so that the more volatile component is transferred from the liquid to the vapour phase, while at the same time the less volatile component is transferred in the reverse direction. When the molar latent heats of the components are equal this mass transfer across the interface is equimolar.

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* The assistance of Dr. H. Sawistowski in writing this chapter is gratefully acknowledged.

Rectification is usually carried out either in plate columns or in packed columns. In the former case the process is evaluated in terms of theoretical plates. The **theoretical plate** is an ideal plate which the vapour and liquid streams leave in equilibrium with one another. The time and area of contact between the two phases should, therefore, be adequate for equilibrium to be approached. The ratio of vapour enrichment obtained by an actual plate to that which would be provided by a theoretical plate is termed the **plate efficiency**. The concept of the theoretical plate has also been applied to simple distillation, although in this case the separation cannot, by the very nature of the process, exceed one theoretical plate.

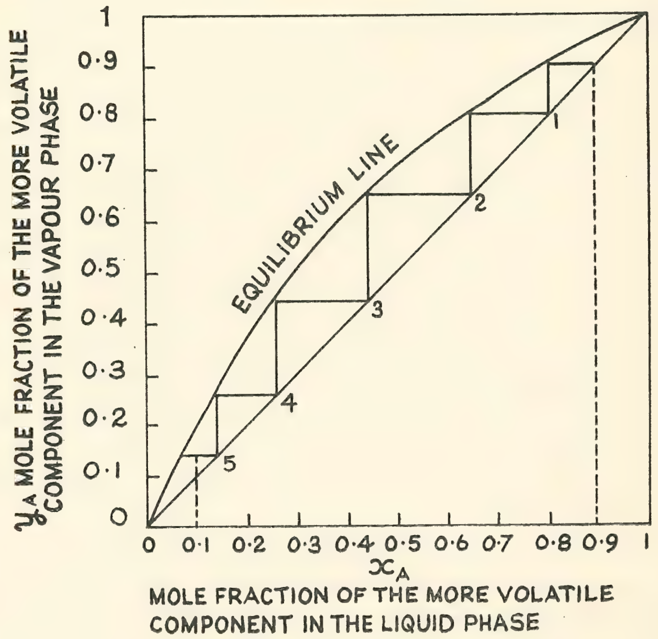


FIG. 13.1 The McCabe–Thiele diagram

The process in packed columns is different in character in that there is a continuous transfer between the phases at all levels of the column and equilibrium cannot be attained at any cross-section. Nevertheless, the idea of a theoretical plate has been applied and the performance expressed as the height equivalent to a theoretical plate (H.E.T.P.), which represents the height of column giving a separation corresponding to one theoretical plate.

The number of theoretical plates required for a given separation is, for a binary mixture, most easily obtained from a McCabe–Thiele diagram. This diagram is obtained by plotting the mole fraction, y, of the more volatile component in the vapour phase versus its mole fraction, x, in the liquid phase (Fig. 13.1). The number of theoretical plates is then determined by drawing steps between the operating and equilibrium lines. The operating line is fixed primarily by the **reflux ratio**, which in English and Continental literature is defined as the *ratio of the liquid returned to the column to the amount of distillate withdrawn* (this definition will be used throughout) and in American literature as the ratio of liquid returned to the column to the vapour leaving it. At total reflux, *i.e.* when no distillate is withdrawn, the operating line coincides with the diagonal and, for a mixture whose equilibrium diagram is given by Fig. 13.1, the number of theoretical plates required to give a top composition of $x = 0{\cdot}9$ and a bottom composition of $x = 0{\cdot}1$ is 5·6. For the determination of the number of theoretical plates at other reflux ratios reference should be made to textbooks on chemical engineering (Coulson and Richardson, CR1; Perry, P13) or monographs on distillation. The same sources will also give methods for calculating plate efficiencies and H.E.T.P.s as well as a selection of experimentally determined values of these quantities. In general, the plate efficiencies vary from 50 to 85% and the H.E.T.P. from 0·5 to 2 ft.

The case of separation of a mixture, *i.e.* the number of theoretical plates required, is determined by the relative volatility of its components. As the term volatility is usually synonymous with activity, a, the relative volatility, α, is defined as:

$$\alpha_{AB} = \frac{a_A}{a_B} = \frac{y_A}{y_B} \times \frac{x_B}{x_A} = \frac{\gamma_A}{\gamma_B} \times \frac{p_A^0}{p_B^0}$$

where γ = the activity coefficient, p^0 is the vapour pressure, and A and B refer to components of the mixture.

Hence, if the system is ideal, *i.e.* $\gamma_A = \gamma_B = 1$, or if the activity coefficients of the two components are equal, the ease of separation depends on the ratio of the vapour pressures of the substances to be separated.

13.2. Distillation at Reduced Pressure

From the point of view of the application of vacuum, distillation can be classified conveniently into:

(*a*) **Distillation at moderate vacuum.**
(*b*) **Unobstructed path distillation.**
(*c*) **Molecular distillation.**

Distillation at moderate vacuum is characterized by the use of conventional distillation equipment and its lower pressure limit is of the order of 1 torr. Unobstructed path and molecular distillation are often classed together as short-path or high-vacuum distillation. They employ the same type of equipment, the difference being one of dimensions and operating conditions. Unobstructed path distillation can be carried out at pressures as low as 10^{-2} torr, whereas in molecular distillation pressures of 10^{-3} torr are frequently in use.

Another useful distinction between the methods of vacuum distillation can be made with reference to the way in which the vapour is formed. This can occur by one of the following mechanisms:

(1) ebullition,
(2) evaporative distillation,
(3) molecular distillation.

Ebullition is usually accompanied by the formation of bubbles when the saturated vapour pressure exceeds the pressure of the surrounding gas. The formation of bubbles and their subsequent movement through the bulk of the liquid in the still creates turbulence, enhances the mass transfer, and thus increases the plate efficiency of the still.

Evaporative distillation occurs when the pressure of the surrounding gas is higher than the vapour pressure of the distilland at a given temperature, so that no bubbles are formed. The rate of evaporation is then controlled by the speed of diffusion or convection of the vapour to the condensing surface; a short path of low impedance from the source to the condenser is therefore desirable. Strictly speaking, distillation by ebullition is always accompanied by a certain amount of evaporative distillation (surface evaporation). At atmospheric pressure this amount is negligible, but its proportion increases with reduction in pressure.

Molecular distillation consists of evaporation into a substantially gas-free space, *i.e.* vacuum. The controlling factor in this case is the rate at which the molecules escape from the heated surface of the distilling liquid which will be referred to as the **distilland**, and are received by the cooled condenser surface. This, in the theoretically simplest case, should be in the immediate vicinity of the evaporating surface. In practice, however, distances of 5 to 10 cm are not harmful provided the mean free path of the residual permanent gases is comparable with or greater than this distance, so that only very few collisions take place between the evaporating molecules and the molecules of the residual gas. This condition is fulfilled when the residual gas has a pressure of 10^{-3} torr, which is easily obtained when the distillands are *moisture-free*.

13.3. Choice of Method of Distillation

Reduced pressure distillation offers several advantages over distillation carried out at atmospheric pressure. The most important are:

(1) use of lower temperatures;
(2) shorter time of thermal exposure of the distilland;
(3) increase in relative volatility;
(4) change in the position of the azeotropic point.

Use of lower temperatures. The use of lower temperatures makes it possible to carry out the distillation of substances which are thermally sensitive and would decompose when distilled at atmospheric pressure. The distillation of dimethyloxyethylphthalate, $C_6H_4(COOC_2H_4OCH_4)_2$ may serve as an example. Owing to the weakness of its molecular bond it decomposes at higher temperatures and so must be distilled at a pressure of 4 torr, which corresponds to a temperature of 198° C. Another advantage in using lower temperatures is the decrease in heat losses and the possibility of utilizing low pressure steam for still-heating. The refining of naphthalene may be considered as an example. At atmospheric pressure the boiling point of naphthalene is 218° C. Hence, steam at about 230° C would have to be supplied for still-heating and this corresponds to a steam pressure of approximately 400 lb/sq in., not often available in chemical plants. However, by carrying out the distillation at 120 torr (boiling point 150° C) a steam pressure of 85 lb/sq in. is sufficient.

Time of thermal exposure. There is a number of substances of high molecular weight like vitamins, hormones, etc., which are thermally unstable even when distilled under high vacuum. However, this thermal hazard can be minimized by reducing the time of thermal exposure. This is best achieved by employing centrifugal or falling-film stills, which will be described later. Table 13.1 (Hickman, H27) gives the average times of exposure for various types of stills at similar throughput per unit area of still.

TABLE 13.1

Still	Approx time of exposure
Laboratory pot still	1–5 hr
Industrial falling-film still	2–10 min
Laboratory falling-film still	10–50 sec
Industrial centrifugal still	0·1–1 sec
Laboratory centrifugal still	0·04–0·08 sec

Recently, Hickmann and Embree (HE1) introduced the concept of a **decomposition hazard**, D, defined as the product of time, t, in seconds and pressure, P, in microns, which is expressed as log D or Dh. Hence

$$Dh = \log D = \log (Pt).$$

A centrifugal still having a time of exposure of 1 sec and operating at 10^{-3} torr will have $Dh = 0$, a conventional pot still distilling for 1 hour at atmospheric pressure will have $Dh = 9{\cdot}44$. It will be noted that in batch operation the thermal exposure of the last fraction is taken into account.

The decomposition hazard scale applies not only to stills but also to the compounds distilled. For example, natural vitamin D will decompose above $Dh = 1$, crude glyceride oil above $Dh = 3$, and stills rated at such levels have to be used for their distillation.

Increase in relative volatility. In general, the ease of separation of a mixture increases with decreasing pressure. Let us consider the separation of citronellal, $C_9H_{17}CHO$ (compound A) and citronellol, $C_{10}H_{19}OH$ (compound B) which is usually carried out by reduced pressure distillation. The vapour pressures, boiling points and relative volatilities $\left(\text{taken as } \frac{p_A{}^0}{p_B{}^0}\right)$ are tabulated in Table 13.2.

As can be seen from the table the relative volatility decreases rapidly with increasing pressure and hence the number of theoretical plates required for a

TABLE 13.2

Pressure, torr	t_A (°C)	$p_B{}^0$ at t_A torr	α at t_A	t_B (°C)	$p_A{}^0$ at t_B torr	α at t_B
5	71·4	1·3	3·57	93·6	15·6	3·12
10	84·8	3·1	3·23	107·0	27·5	2·75
20	99·8	7·2	2·86	121·5	49·6	2·48
40	116·1	15·6	2·56	137·2	90·3	2·26
60	126·2	25·0	2·40	147·2	127·2	2·12
100	140·1	45·2	2·21	159·8	199·8	2·00
200	160·0	102	1·96	179·8	360	1·80
400	183·8	228	1·76	201·0	655	1·64
760	206·5	477	1·59	221·5	1126	1·48

given separation will increase. An indication of it can be obtained by considering the separation achieved at total reflux. The number of plates required at total reflux is given by Fenske's equation (Fenske, F12),

$$N_{TP} = \frac{\log \left(\frac{x_A}{x_B}\right)_t \left(\frac{x_B}{x_A}\right)_s}{\log \alpha_{\text{aver}}}$$

where the subscripts t and s refer to top and bottom of the column. Hence, in order to obtain a separation from $(x_A)_s = 0{\cdot}05$ to $(x_A)_t = 0{\cdot}95$ the number of theoretical plates, N_{TP}, required at 10 torr is

$$N_{TP} = \frac{\log \left(\frac{95}{5} \times \frac{95}{5}\right)}{\log \frac{3{\cdot}23 + 2{\cdot}75}{2}} = \frac{2 \log 19}{\log 2{\cdot}99} = 5{\cdot}4.$$

The corresponding figures for 100 and 760 torr are 7·9 and 13·7.

It has to be pointed out that the above considerations apply only to distillation at moderate vacuum as they are based on phase equilibria. Unobstructed path or molecular distillation are intrinsically non-equilibrant processes and, as will be shown later (§ 13.5), the quantities of constituents distilling are not proportional to their partial pressure p_i but to $\frac{p_i}{\sqrt{M_i}}$, where M_i is the molecular weight. However, since substances of similar molecular weight encountered in natural mixtures usually distil at similar temperatures, the kind of separation achieved in high vacuum distillation does not differ much from the separation obtained in simple equilibrium distillation. Hence, the concept of a theoretical plate can also be applied to it but it is then called a **theoretical molecular plate** (T.M.P.).

Behaviour of azeotropes. In nearly all systems forming azeotropes at atmospheric pressure a reduction in pressure causes the azeotrope to become richer in the more volatile component. This is evident from Table 13.3 giving the azeotropic composition and the azeotropic boiling point as a function of pressure for the system ethanol-water. No azeotrope is being formed below 70 torr.

TABLE 13.3

Pressure (torr)	Azeotropic content of H_2O by wt	Azeotropic content of H_2O mole %	Azeotropic b. pt (°C)
70	0	0	27·96
94	0·5	1·3	33·35
129	1·3	3·3	39·20
298	2·7	6·6	47·63
404	3·75	9·1	64·04
760	4·4	10·5	78·15
1075	4·65	11·0	87·12
1451	4·75	11·3	95·35

This change in the position of the azeotropic point can be utilized for separation of azeotropic mixtures by the combination of vacuum and normal distillation. With reference to Fig. 13.2, which represents the McCabe–Thiele diagram of the mixture considered, let x_1 be the initial composition of the mixture and x_3 the required composition of the product. Point C is the azeotropic point at a pressure p_1 and point D the azeotropic point at a pressure p_2, where $p_1 > p_2$. The first distillation is carried out at pressure p_2 in such a way that a product is obtained of a composition intermediate between C and D, say x_2. This product is then redistilled at pressure p_1 to give a final product of the required degree of purity.

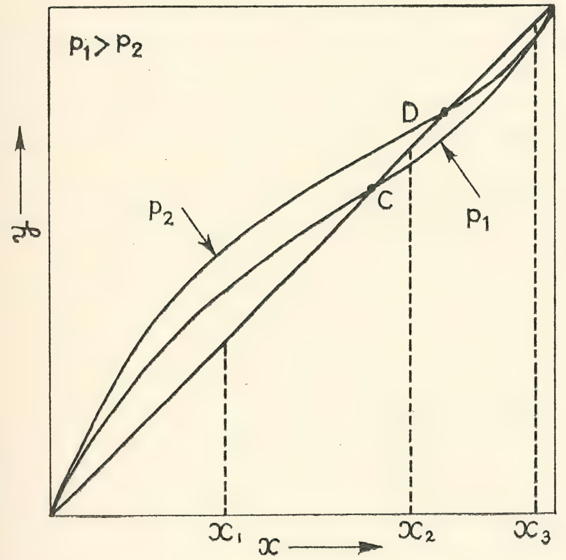


FIG. 13.2 Separation of azeotropes

It has to be realized that it is not possible to predict from fundamental considerations which method of distillation should be applied to a given substance to obtain the most satisfactory results as far as quality and cost are concerned. Even though many substances can be distilled at atmospheric pressure, it may be preferable, from the standpoint of energy consumption, to distil them at reduced pressure.

In general, reduced pressure distillation is used mainly for liquids having molecular weights over 200 and boiling points above 200° C at atmospheric pressure. Of the great number of substances which are processed industrially at reduced pressure distillation a few examples are: coal tar, lubricating oils, transformer oils, vegetable oils, whale oil, glycerine and high boiling esters for use as plasticizers.

13.4. Distillation at Moderate Vacuum

The principles of distillation at moderate vacuum do not differ from those of ordinary distillation and the methods of equipment design are similar. The only significant difference is in the approach to the problem of pressure drop. It is of secondary importance in ordinary distillation, but in many reduced pressure distillations it becomes a critical factor as far as size and shape of equipment are concerned.

Large-scale industrial distillations at moderate vacuum are mainly conducted in plate or packed columns. Plate columns are preferred for larger throughputs (column diameter above 2 ft) at lower vacuum; packed columns for relatively higher vacua since, at equal performance, they have lower pressure drop than plate columns and also if the column diameter is less than 2 ft.

Pressure drop in packed columns. The pressure drop in packed columns can be calculated from a modified form of the Colburn equation (Chilton and Colburn, CC1).

$$\Delta p = 2f \frac{Z}{d_p} \frac{G^2}{g(\rho_G)_{\text{av}}} C_h C_L$$

where Δp = pressure drop,
f = friction factor,
Z = height of packing,
d_p = diameter of packing elements,
$G = u\rho_G$ = mass flow of vapour,
ρ_G = density of vapour,
u = superficial vapour velocity,
g = acceleration due to gravity,
C_h = correction factor for hollow packings,
C_L = correction factor for liquid flow.

The friction factor, f, is given by the equations

$$f = \frac{38}{Re^{0\cdot 15}} \quad \text{if } Re > 40$$

and

$$f = \frac{850}{Re} \quad \text{if } Re < 40,$$

where $Re = \dfrac{d_p \rho_G u}{\eta_G}$ = Reynolds number and

η_G = viscosity of vapour.

The vapour density, $(\rho_G)_{\text{av}}$, is the arithmetic average of the densities at top and bottom of the column. As the conditions at the top of the column are initially unknown, the equation has to be solved by trial and error. The correction factor C_L can be taken as unity since in reduced pressure distillation the density of liquid flow is low.

The correction factor C_h is equal to unity for solid packings of void fraction between 0·35 and 0·45. For Raschig rings it is given by the equation $C_h = \dfrac{0\cdot 24}{\sqrt{d'p}}$, where $d'p$ is the nominal packing diameter in inches (Perry, P13)

For other types of packing it might be preferable to use different correlations like Carman's (Carman, C6) or Brownell's (Brownell and Katz, BK2; Brownell, Dombrowski and Dickey, BDD1) but these involve the knowledge of void fraction and specific surface of packing.

The equation is derived from its differential form by assuming that the density is a function of pressure alone, *i.e.* that the variations in density due to changes in temperature along the column are small. This is justified in most cases and the error introduced is usually small and gives an answer on the safe side.

Flooding velocities in packed columns. The variation of vapour density with column weight affects also the flooding velocity. The flooding velocity, u_f, is given either by the graphical correlation of Lobo *et al.* (Lobo, Friend, Hashmal, and Zenz, LFHZ1) or by the equation (Sawistowski, *private communication*):

$$ln\left[\frac{u_f{}^2 S\, \rho_G}{g\varepsilon^3\, \rho_L}\left(\frac{\eta_L}{\eta_W}\right)^{0\cdot 2}\right] = -4\left(\frac{L}{G}\right)^{\frac{1}{4}}\left(\frac{\rho_G}{\rho_L}\right)^{\frac{1}{8}}$$

where S = surface area of packing per unit volume of packed bed,
ε = void fraction,
ρ_L = liquid density,
η_L = liquid viscosity,
η_W = viscosity of water at 20° C = 1 centipoise.

By mathematical analysis of the above equation it can be shown that the critical flooding conditions exist at the top of the column. As the top conditions are unknown, it is recommended to base the design calculations on the bottom conditions but taking the operating velocity as 50% of the flooding velocity instead of the customary 60–75% and later checking the calculations for the top conditions. This method of approach will be illustrated in the following example.

Example. *Cinnamylaldehyde* ($C_6H_5CH{=}CHCHO$) *is to be purified in a column packed with* $\frac{1}{4}$ *in. stoneware Raschig rings. Owing to its thermal sensitivity the distillation has to be carried out below 140° C. A product rate of 225 lb/hr is required. Laboratory tests have shown that at a reflux ratio of 8, a column 5 ft high is necessary to give the required purity of the product. Calculate the column diameter and the suction pressure of the vacuum pump. The estimated values of the physical properties are* $\rho_L = 1{\cdot}0$ *g/cm*^{3}, $\eta_L = 0{\cdot}25$ *centipoise,* $\eta_V = 0{\cdot}008$ *centipoise.*

Solution. From table of vapour pressures (Stull, S28) it is found that the temperature of 140° C corresponds to a pressure of 24 torr, assuming that the presence of impurities does not alter the boiling point significantly. This pressure has to be maintained in the still.

(*i*) Calculation of the flooding velocity at the bottom of the column. The flooding velocity is calculated from the formula

$$\frac{u_f{}^2 S}{g\varepsilon^3}\cdot\frac{\rho_G}{\rho_L}\left(\frac{\eta_L}{\eta_W}\right)^{0\cdot2}=e^{-4\left(\frac{L}{G}\right)^{\frac{1}{4}}\left(\frac{\rho_G}{\rho_L}\right)^{\frac{1}{8}}}$$

From tables (Coulson and Richardson, CR1): $S = 242$ ft²/ft³ and $\varepsilon = 0\cdot72$. Since the reflux ratio is $R = 8$ therefore

$$\frac{L}{G}=\frac{R}{R+1}=\frac{8}{9}=0\cdot889 \text{ and } \left(\frac{L}{G}\right)^{\frac{1}{4}}=0\cdot971$$

$$\rho_G=\frac{M}{22414}\cdot\frac{T_0}{T}\cdot\frac{p}{p_A}=\frac{132}{22414}\frac{273}{760}\frac{P}{T}=21\cdot2\times10^{-4}\frac{P}{T}$$

where M = molecular weight = 132,
p = operating pressure in torr,
T = temperature in °K.

$$(\rho_G)_S=21\cdot2\times10^{-4}\frac{24}{414}=1\cdot230\times10^{-4}\text{ g/cm}^3$$

$$\left(\frac{\rho_G}{\rho_L}\right)_S^{\frac{1}{8}}=1\cdot23^{\frac{1}{8}}\times10^{-\frac{1}{2}}=0\cdot324$$

$$\therefore\quad 4\left(\frac{L}{G}\right)^{\frac{1}{4}}\left(\frac{\rho_G}{\rho_L}\right)_S^{\frac{1}{8}}=4\times0\cdot971\times0\cdot324=1\cdot260 \text{ and } e^{-1\cdot26}=0\cdot283$$

$$u_f{}^2=0\cdot283\,\frac{g\varepsilon^3}{S}\,\frac{\rho_L}{\rho_G}\left(\frac{\eta_W}{\eta_L}\right)^{0\cdot2}=0\cdot283\,\frac{32\cdot2\times0\cdot72^3}{242}\times\frac{10^4}{1\cdot23}\left(\frac{1}{0\cdot25}\right)^{0\cdot2}=151$$

$$\therefore\quad (u_f)_s=12\cdot3\text{ ft/sec.}$$

(*ii*) Estimation of the column cross-section, *A*.

Since the product rate is 2·25 lb/hr and the reflux ratio 8, hence the vapour rate is $(R + 1) \times 2\cdot25 = 9 \times 2\cdot25 = 20\cdot25$ lb/hr. By taking the operating velocity at column bottom as 50% of the bottom flooding velocity we have $u_S = 0\cdot5(u_f)_s = 6\cdot15$ ft/sec.

$$A=\frac{20\cdot25}{3600\,u_s(\rho_G)_s}=\frac{20\cdot25\times10^4}{3600\times6\cdot15\times1\cdot23\times62\cdot4}=0\cdot119\text{ ft}^2=17\cdot1\text{ in.}^2$$

$$\therefore\quad \text{Column diameter}=D=2\sqrt{\frac{A}{\pi}}=2\sqrt{\frac{17\cdot1}{\pi}}=4\cdot67\text{ in., say } D=5\text{ in.}$$

and

$$A=\frac{\pi D^2}{4}=\frac{\pi\times25}{4\times144}=0\cdot136\text{ ft}^2.$$

(*iii*) Calculation of pressure drop.

$$G=\frac{20\cdot25}{0\cdot136}=149\text{ lb/hr ft}^2.$$

$$Re=\frac{Gd_p}{\eta_G}=\frac{1\cdot49\times0\cdot25}{12\times0\cdot008\times2\cdot42}=160>40$$

$$f=\frac{38}{Re^{0\cdot15}}=\frac{38}{160^{0\cdot15}}=17\cdot8$$

First trial.

Let $\Delta p = 12$ torr. Then $p_t = 12$ torr and $t_t = 125°$ C

$$(\rho_G)_t=21\cdot2\times10^{-4}\frac{p_t}{T_t}=21\cdot2\,\frac{12}{398}\,10^{-4}=0\cdot639\times10^{-4}\text{ g/cm}^3$$

$$(\rho_G)_{\text{av}}=\frac{1\cdot230+0\cdot639}{2}\,10^{-4}=0\cdot935\times10^{-4}\text{ g/cm}^3=5\cdot84\times10^{-3}\text{ lb/ft}^3$$

$$\Delta p=2f\,\frac{Z}{dp}\,\frac{G^2}{g(\rho_G)_{\text{av}}}\,C_hC_L,\text{ where } C_h=\frac{0\cdot24}{\sqrt{d'p}}=0\cdot48\text{ and } C_L=1.$$

$$\therefore\quad p_1=2\times17\cdot8\times5\times48\left(\frac{149}{3600}\right)^2\frac{0\cdot48}{32\cdot2}\left(\frac{10^3}{5\cdot84}\right)=37\cdot4\text{ lb/ft}^2$$

$$=0\cdot260\text{ lb/sq in.}=13\cdot4\text{ torr}\qquad \textit{No check.}$$

Second trial.

Let $\Delta p = 14$ torr. Then $p_t = 10$ torr and $t_t = 120°$ C.

$$(\rho_G)_t=21\cdot2\times10^{-4}\frac{10}{393}=0\cdot540\times10^{-4}\text{ g/cm}^3$$

$$(\rho_G)_{\text{av}}=\frac{1\cdot230+0\cdot540}{2}\,10^{-4}=0\cdot885\times10^{-4}\text{ g/cm}^3=5\cdot52\times10^{-3}\text{ lb/ft}^3$$

$$\Delta p_2=\Delta p_1\frac{(\rho_G)_{\text{av}\,1}}{(\rho_G)_{\text{av}\,2}}=13\cdot4\times\frac{5\cdot84}{5\cdot52}=14\cdot2\text{ torr.}\quad \textit{Check.}$$

(*iv*) Calculation of flooding velocity at top of column.

$$\left(\frac{\rho_G}{\rho_L}\right)_t^{\frac{1}{8}}=\frac{0\cdot540^{\frac{1}{8}}}{10^{\frac{1}{2}}}=\frac{0\cdot926}{3\cdot162}=0\cdot293$$

$$4\left(\frac{L}{G}\right)^{\frac{1}{4}}\left(\frac{\rho_G}{\rho_L}\right)^{\frac{1}{8}}=4\times0\cdot971\times0\cdot293=1\cdot138\text{ and } e^{-1\cdot138}=0\cdot321.$$

$$(u_f)_t{}^2=(u_f)_s{}^2\,\frac{0\cdot321}{0\cdot283}\times\frac{(\rho_G)_s}{(\rho_G)_t}=151\times\frac{0\cdot321}{0\cdot283}\times\frac{1\cdot230}{0\cdot540}=390$$

$$\therefore\quad (u_f)_t=19\cdot7\text{ ft/sec.}$$

(*v*) Calculation of the actual velocity at column top.

$$u_t=\frac{G}{3600(\rho_G)_t}=\frac{149\times10^4}{3600\times0\cdot540\times62\cdot4}=12\cdot3\text{ ft/sec.}$$

$$\therefore\quad u_t=0\cdot625\,(u_f)_t$$

Hence, a column 5 in. in diameter and a vacuum pump capable of reducing the pressure to 10 torr are satisfactory.

Equilibrium data. The equilibrium data can be determined experimentally or, if available, taken from literature. In cases, however, where the compounds distilled are of a similar nature, they can be calculated on the basis of Raoult's law. Since from Dalton's law $p_i = y_i p$ and, according to Raoult's law $p_i = p_i^0 x_i$

hence
$$y_i = \frac{p_i^0}{p} x_i$$

where p_i^0 = vapour pressure of pure component i at temperature t,
p_i = partial pressure of component i,
p = total pressure.

The equilibrium data can, therefore, be calculated by trial and error assuming various temperatures t until $\Sigma y_i = 1$.

Example. *Calculate the equilibrium data for the system citronellal–citronellol at 10 torr using the vapour pressure data given in Table 13.2. (For this purpose it is best to plot the vapour pressure data as log* p_i^0 *against* t.)

Solution. The method of approach will be shown only for $x_A = 0{\cdot}1$. Let cintronellal be component A and citronellol component B.

First trial.

Let $t = 104°$ C. Then $p_A^0 = 24{\cdot}2$ torr and $p_B^0 = 8{\cdot}7$ torr

$$y_A = \frac{p_A^0}{p} x_A = \frac{24{\cdot}2}{10} 0{\cdot}1 = 0{\cdot}242$$

$$y_B = \frac{p_B^0}{p} x_B = \frac{8{\cdot}7}{10} 0{\cdot}9 = 0{\cdot}783$$

$\Sigma y = 1{\cdot}025$. *No check.*

Second trial.

Let $t = 103{\cdot}5°$ C. Then $p_A^0 = 23{\cdot}8$ torr and $p_B^0 = 8{\cdot}5$ torr.

$$y_A = \frac{23{\cdot}8}{10} 0{\cdot}1 = 0{\cdot}238$$

$$y_B = \frac{8{\cdot}5}{10} \times 0{\cdot}9 = 0{\cdot}765$$

$\Sigma y = 1{\cdot}003$. *No check.*

By interpolation $t = 103{\cdot}4°$ C, $y_A = 0{\cdot}237$, $y_B = 0{\cdot}763$.

In a similar way the values of y_A and t are calculated for other values of x_A and the results are collected in Table 13.4.

TABLE 13.4

x_A	0·1	0·2	0·4	0·6	0·8	0·9
y_A	0·237	0·416	0·660	0·824	0·926	0·966
t	103·4	100·8	95·8	91·3	88·1	86·5

The equilibrium data are plotted in Fig. 13.3 and in order to illustrate the point of increased ease of separation with increasing vacuum (§ 13.3) the data at 100 and 760 torr are also included.

Large-scale industrial stills. Figure 13.4 shows the diagram of a reduced pressure distillation plant, for example, used in the refining of naphthalene, in which the vacuum is produced by a steam-ejector pump. The use of a forced circulation external reboiler has been found more satisfactory than ordinary steam heating by means of coils as it prevents bumping and ensures a more steady operation. Nevertheless, steam coils are installed in the still as an emergency measure to prevent the soldification of the charge should the re-circulation pump or the steam supply to the reboiler break down. The cooling water supply to the condenser must be preheated to above 80° C or alternatively subcooled steam condensate can be employed to prevent solidification of naphthalene in the condenser. The purpose of the interceptor is to remove entrained naphthalene and thus prevent blockage of the ejector. In practice, plants of this type can handle up to 50 tons of material with a batch cycle up to 100 hours.

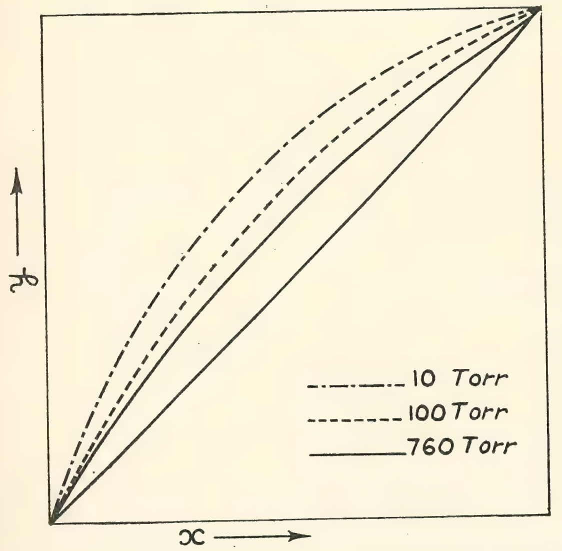


FIG. 13.3 Equilibrium diagram of the system citronellal–citronellol

Figure 13.5 illustrates another type of an industrial still in which a gas-ballast rotary pump is used. In this case a steam-jacketed still provided with a stirrer is employed. This type of equipment is satisfactory only for smaller stills as the ratio of heating surface to volume of liquid becomes progressively unfavourable with an increase in still size. In order to compensate for this effect, steam at a higher pressure, *i.e.* at higher temperature, would have to be used, thus increasing the danger of decomposition, particularly when the liquid does not cover the whole heating surface.

Small-scale stills. For low throughputs and lower pressures, when the pressure drop in the column becomes excessive, simple distillation is employed and the equipment used closely resembles ordinary laboratory distillation trains. It consists usually of a pot still and a condenser, their mutual arrangement and design depending upon the working pressure. Fig. 13.6 shows an ordinary laboratory distillation flask which is satisfactory for distillations down to 15 torr. In order to decrease bumping, a few pieces of pumice are introduced into the still. A water-jet pump is used to produce the vacuum.

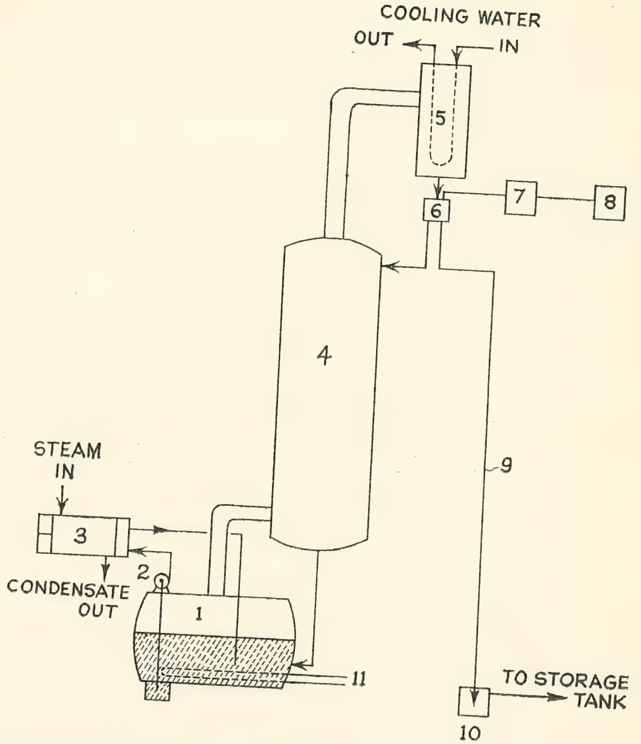

COOLING WATER
OUT
IN
5
6
7
8
4
STEAM IN
3
CONDENSATE OUT
2
1
9
11
TO STORAGE TANK
10

FIG. 13.4 Reduced pressure distillation plant used for refining of naphthalene and utilizing a steam-ejector pump

1, Still; 2, recirculation pump; 3, external reboiler; 4, column (20 plates); 5, total condenser; 6, reflux split-box; 7, interceptor; 8, steam-ejector pump; 9, barometric leg; 10, seal pot; 11, emergency steam coil

At lower pressures, obtained by a gas-ballast pump, the design of the apparatus becomes of greater importance. The vapour lines are made wider and shorter and the Liebig condenser dispensed with. The problem created by pumping is sometimes obviated by **entrainer distillation.** This is shown in Fig. 13.7, the apparatus being a modified form of the Claisen flask. It is provided with a fine, hairlike capillary through which inert gas, *e.g.* hydrogen, is introduced. A side tube of 1 cm dia is recommended for a still pot 10 cm in diameter. The collecting flask serves also as a condenser.

Rotating stills. At the reduced pressure used in the above stills the liquid evaporates without truly boiling, *i.e.* there is a much reduced formation of bubbles compared with that which would occur at atmospheric pressure. This

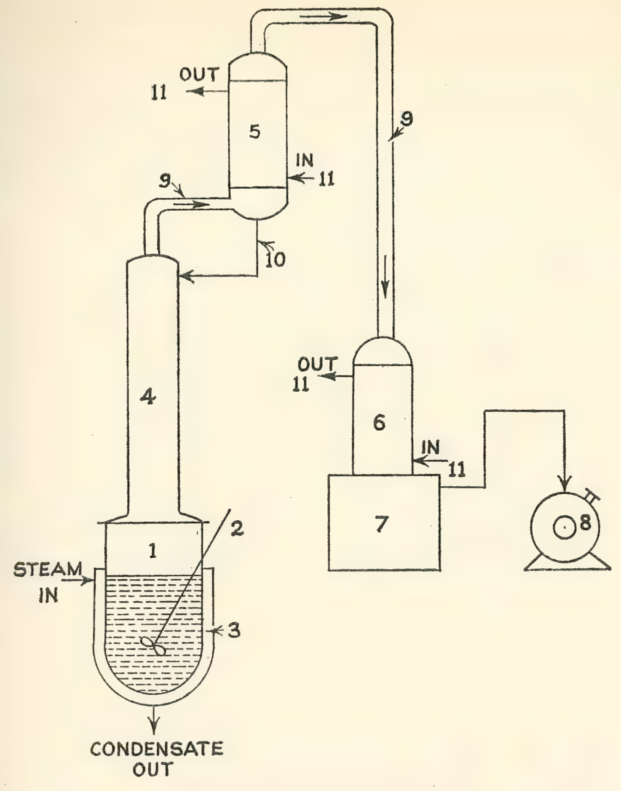

11
OUT
5
IN
11
9
9
10
4
OUT
11
6
IN
11
7
8
2
1
STEAM IN
3
CONDENSATE OUT

FIG. 13.5 Reduced pressure distillation plant utilizing gas-ballast pump

1, Still; 2, stirrer; 3, steam jacket; 4, rectification column; 5, partial condenser; 6, total condenser; 7, distillate receiver; 8, gas-ballast pump; 9, vapour line; 10, reflux line; 11, cooling water connections

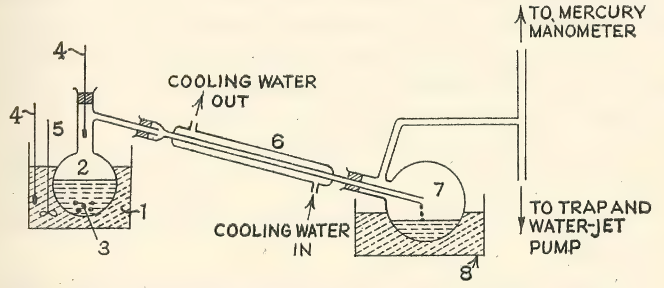

TO MERCURY MANOMETER
4
4
5
COOLING WATER OUT
6
2
1
3
COOLING WATER IN
7
8
TO TRAP AND WATER-JET PUMP

FIG. 13.6 Ordinary laboratory vacuum distillation assembly

1, Heating bath; 2, distillation flask; 3, pieces of pumice; 4, thermometers; 5, stirrer; 6, Liebig condenser; 7, collecting flask; 8, cooling bath phenomenon becomes more pronounced the lower the pressure and is accompanied by an increased tendency towards bumping. Agitation of the distilland in the still is therefore small and heat transfer is poor, particularly if the depth of the liquid is too great. This defect may be partly overcome by the use of forced circulation reboilers, stirring or gas entraining. However, since the evaporation takes place only from the surface of the liquid, it is advisable to make this surface as large as possible by spreading it into a thin film.

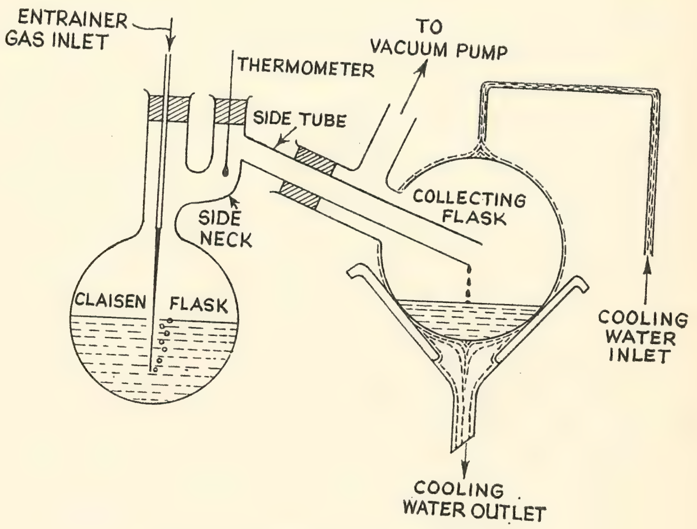


Fig. 13.7 Entrainer distillation

This technique will be discussed chiefly in the section on molecular distillation (§ 13.5) though it is nowadays in common use in all types of distillation where no ebullition occurs. Fig. 13.8 illustrates schematically an industrial vacuum distillation apparatus which can also be used for vacuum evaporation. A film of the distilland is spread over the surface of a heated drum, 1, from which it evaporates. The spreading is achieved by a transfer roller, 4, which rotates in a container, 3, filled with the distilland. The distilland is fed continuously into this container by a circulating pump, 11, from a tank, 9, (provided with a heater, 10, to keep the distilland warm and so lower its viscosity). Means for keeping the liquid level constant are provided, but are only indicated in the diagram. A scraper, 6, and a waste disposal worm extruder are useful accessories. The container, 2, can be evacuated to the pressure required.

One of the main problems of this type of evaporator is the heat transfer to the film. This has been discussed in detail in a paper by Kramers, van Cappelle and van der Schraaf (KCS1).

Accessories. The necessary vacuum equipment includes steam ejector pumps, single or multi-stage (§ 2.18) according to the working pressure required. If no steam is available, water-seal pumps, gas-ballast pumps (§ 2.5) together with a variety of condensers and traps are used. For the measurement of pressure, Bourdon type manometers, preferably with barometric correction (§ 3.3), mercury manometers and the Alphatron gauge (§ 3.11) can be employed. In place of mercury in a manometer, butyl phthalate or sulphuric acid are often convenient.

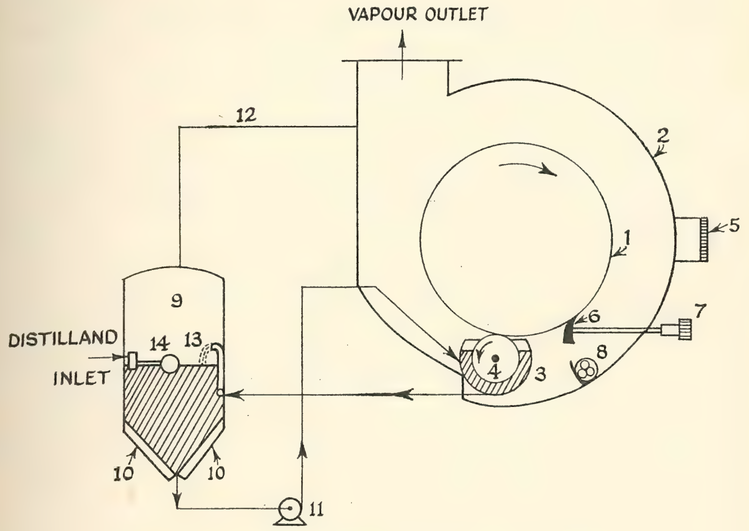


Fig. 13.8 A rotating, spread-film evaporator

1, Hot rotating cylinder; 2, evacuated container; 3, distilland container; 4, transfer roller; 5, window; 6, scraper; 7, scraper adjustment; 8, waste disposer; 9, distilland reservoir; 10, heater; 11, circulating pump; 12, pressure equalizing line; 13, level adjuster of distilland in 3; 14, ball float valve

13.5. Molecular Distillation

From the standpoint of vacuum technology, molecular distillation is the most interesting and up-to-date technique. Since the distilling molecules pass directly from the vaporizing surface to the condenser there is no possibility for a dynamic equilibrium to be established between the vapour and the liquid. Consequently, there exists no definite temperature at which the distillation starts and it will take place always when there is a temperature gradient between the evaporating surface and the condenser.

By definition, molecular distillation implies distillation within the mean free path of the molecules, to reduce the number of collisions between the vapour molecules and the residual gas molecules and hence to avoid delay in vapour molecules reaching the condenser and eliminate the possibility of their return to the evaporating surface. Theoretical considerations and experimental results indicate, however, that heavy molecules, *e.g.* molecules of plasticizer oils, suffer only small deflections when they collide with air molecules because of their large masses and because the air molecules only strike one or two of the outermost hydrogen atoms of the heavy molecules.

The hydrogen atoms rebound freely on impact, so that the momentum transferred and therefore the deflection of the heavy molecule from its path, are small (Jacobs and Kapff, JK1). Hence, the actual vapour pressures may easily be a few orders of magnitude higher than the residual gas pressure (Morse, M18; Pirani, P14). Also an increase in the pressure of the residual gas, which results in an increased number of collisions, matters less than originally supposed. This point is best illustrated by Table 13.5 (Perry, P13; Hickman, H28).

TABLE 13.5

Pressure of residual air in 2 cm gap, micron	2 cm gap is multiple m of mean free path	Rate of distillation per m² of distilland surface of falling-film still at saturation pressures						No. of molecules reaching condenser without collision
		1 micron		3 micron		10 micron		
		g/sec	%	g/sec	%	g/sec	%	
0·3	$m = 0{\cdot}2$	0·6	100	1·85	100	6·4	100	80
4·0	3	0·46	77	1·59	86	5·7	89	
7	5	0·38	63	1·37	74	5·2	81	
10	7	0·32	53	1·18	64	4·6	72	0·005
25	17	0·21	35	0·70	38	2·1	42	
50	33	0·12	20	0·40	22	1·67	27	

The maximum amount of distilland N which can be evaporated and then condensed at the receiver surface in molecular distillation is expressed by the Langmuir–Knudsen interpretation of the Maxwell–Boltzmann law

$$N = \frac{pA}{\sqrt{2\pi M \mathbf{R} T}}$$

where p = vapour pressure in dyne cm^{-2},
A = area of evaporator surface in cm^2,
M = molecular weight of the distilland,
$\mathbf{R}$ = gas constant, $= 8{\cdot}314 \times 10^7$ erg deg^{-1} C. mole^{-1},
T = absolute temperature in °K.

For practical calculations of M_a, the mass transfer per cm² of distilland surface, the equation is:

$$M_a = \frac{N}{A} = 0{\cdot}0583 p \sqrt{\frac{M}{T}} \left(\frac{\text{g}}{\text{cm}^2\ \text{sec}}\right)$$

where p is in torr.

Thus, in the case of a liquid of molecular weight 350 and undergoing distillation at a surface temperature of 450° K, the mass transferred is

$$M_a = 0{\cdot}5 \text{ mg/cm}^2 \text{ sec approx.}$$

This figure gives the maximum mass transfer obtainable from a molecular still having one theoretical molecular plate. In practice, about 0·8 to 0·9 of this figure is obtainable from well-designed molecular stills (Hickman, H29), whereas ordinary laboratory pot stills may achieve 0·3 to 0·5 T.M.P.

The Langmuir–Knudsen equation implies that, in the case of mixtures, the maximum rate of distillation of component i at a given temperature is proportional to $\frac{p_i}{\sqrt{M_i}}$, where p_i is the partial pressure of the constituent.

Hence, in any distilled fraction each constituent will appear in a certain amount, the relative quantities of the constituents being proportional to $\frac{p_i}{\sqrt{M_i}}$. If the fractions are withdrawn at equal time intervals and at uniform temperature increments, the yield of each constituent will follow a smooth probability curve as shown in Fig. 13.9. These curves are often referred to as elimination curves and they are of great importance in analytical distillation (Hickman, H30; Embree, E9).

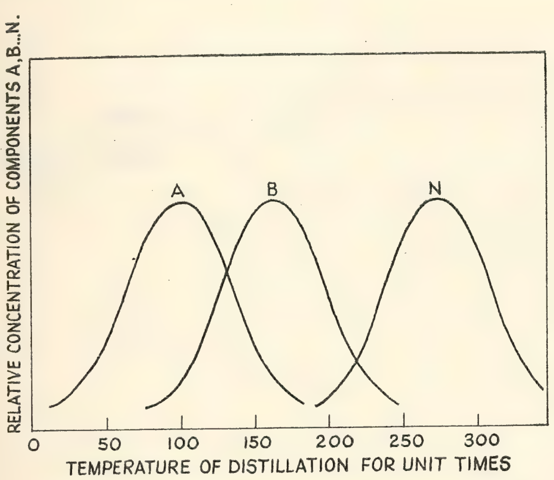


FIG. 13.9 Theoretical elimination curves

Laboratory type molecular still. A readily constructed model is shown in Fig. 13.10. C is the container for the distilland D, and S is the delivery tube. Passing through the neck of C is the water-cooled condenser tube W. This tube is bent upwards slightly within the bulb of the container C, where the molecular distillation takes place. This condenser tube is provided with a drip point P which, together with the upwards inclined tube end, has the function of directing the condensed liquid into the distillate receiver R. The heater H—electric or gas—heats the high boiling liquid contained in the metal bowl M, the temperature of which is measured by orthodox means.

It will be appreciated that the molecular distillation as described is a slow batch process and not easily converted to a speedy, continuous method suitable for large-scale working. A faster process is necessary for several reasons, the most obvious being the economic one. Transferring molecules from a free surface to a nearby condensing surface is bound to be costly, especially if the transfer is done from a liquid surface at low vapour pressure, often necessary to avoid damage to the distilland. Again, a higher speed is desirable for physico-chemical reasons: the decomposition probability increases rapidly with the time which elapses while the surface is at the required temperature. Furthermore, the danger of decomposition will increase with thickness of the liquid layer because, in order to bring the surface to a certain temperature, a temperature gradient must exist, with a higher temperature at the bottom of the layer.

Thus two main design problems arise: (*i*) the distilland must be spread in a very thin even layer over a large hot surface from which it evaporates quickly; (*ii*) the liquid film must be replaced continuously.

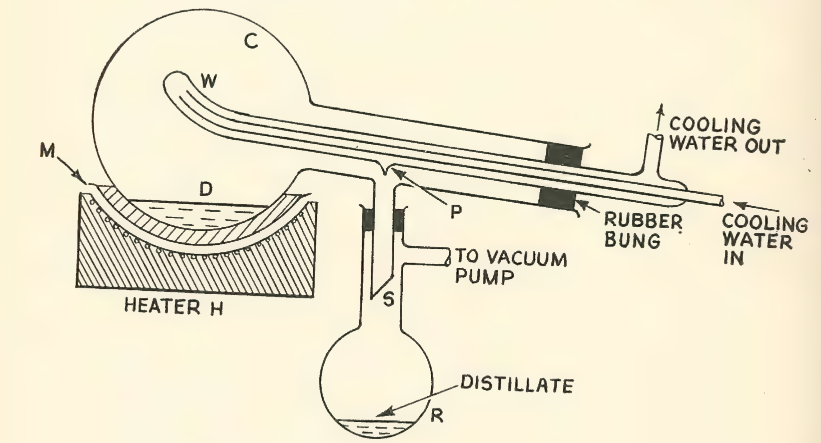

C
W
M
D
P
S
R
COOLING WATER OUT
RUBBER BUNG
COOLING WATER IN
TO VACUUM PUMP
HEATER H
DISTILLATE

FIG. 13.10 Laboratory type molecular still

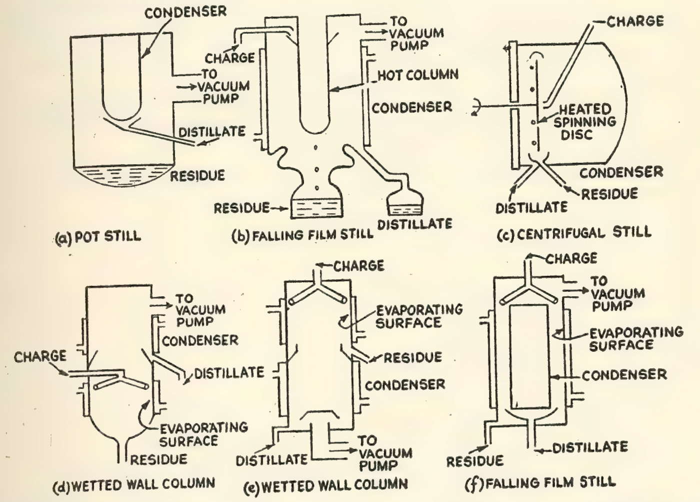
It has proved to be practical to evaporate about half of the film in each 'evaporation period' and then replace it by a fresh film. This period, with films about 10^{-2} mm to 10^{-1} mm in thickness, is of the order of 2×10^{-2} sec to 60 sec, depending on the design of the still.

The decomposition hazard may vary by as much as 1 to 3000 for molecular stills with continuously changing film, and it will be about 150,000 for a laboratory still of a type like that of Fig. 13.10.

The properties of a given material present in a fraction of the distillate can be indicated by the use of pilot dyes, which evaporate together with the distilland. The final colour of the distillate is a measure of the distilland fraction (Davy, D11).

Further types of molecular still. Various molecular stills are illustrated by Fig. 13.11. Fig. 13.11(*a*) depicts an alternative design of laboratory pot still to that of Fig. 13.10. Figure 13.11(*b*) shows a **falling film molecular still.** In this pattern, the distilland (charge) is spread over the surface of the hot column and evaporates from it on to the cooled condenser. The distillate is collected and the residue—which has a lower vapour pressure—drips down into the residue collector. In order to form a film, it is obvious that the distilland must wet the hot column. In most cases this is achieved, though there are certain higher alcohols which do not wet glass, and other liquids which might not wet certain metals. There is no method of predicting the film-forming behaviour of a substance on a given surface other than by preliminary experimentation. Methods of surface conditioning, beyond the scope of the present work, may be adopted to overcome this difficulty.

Providing film formation takes places, the time during which the film is exposed to the hot surface is controlled by the volume density and viscosity of the liquid. Viscous liquids of low density will form thicker films and flow slowly. There is no method of influencing the time of exposure at a given temperature in a falling film still.


CONDENSER
CHARGE
TO VACUUM PUMP
DISTILLATE
RESIDUE
TO VACUUM PUMP
HOT COLUMN
CONDENSER
RESIDUE
DISTILLATE
CHARGE
HEATED SPINNING DISC
CONDENSER
RESIDUE
DISTILLATE
CHARGE
TO VACUUM PUMP
CONDENSER
CHARGE
DISTILLATE
EVAPORATING SURFACE
RESIDUE
EVAPORATING SURFACE
RESIDUE
CONDENSER
DISTILLATE
TO VACUUM PUMP
CHARGE
TO VACUUM PUMP
EVAPORATING SURFACE
CONDENSER
RESIDUE
DISTILLATE

(*a*) POT STILL (*b*) FALLING FILM STILL (*c*) CENTRIFUGAL STILL
(*d*) WETTED WALL COLUMN (*e*) WETTED WALL COLUMN (*f*) FALLING FILM STILL

FIG. 13.11 Molecular stills for laboratory and industrial applications (*from* 'High vacuum distillation', *Chemistry and Industry*, 1948, p. 516, Fig. 7)

As the evaporation takes place from the surface, the film has to be 'stirred' in order to keep it homogeneous. Four factors will help to attain this end: the diffusion; the circulation due to temperature differences in the film; the turbulence, which may be controlled by the shape and structure of the surface (*e.g.* use of grooves); and the use of mechanical movable obstacles.

The total transport of material to the surface due to diffusion is governed by the diffusion constant of the liquid, the difference in concentration between the 'deeper' strata and the surface, the film thickness (order of 10^{-2} to 10^{-1} mm) and the surface area.

To obtain a large throughput and a low risk of dissociation, necessary with certain materials, a much thinner film than that in the falling film still must be achieved, so that quick evaporation with less time in contact with the hot surface is attained. A method used is to feed the distilland on a rapidly rotating disc of which the temperature is raised by a nearby radiant heater, in the so-called **centrifugal still** (Fig. 13.11)*c*)). Using a disc of about 200 cm dia a speed of about 400 r.p.m. is usual. Up to 5000 r.p.m. may be used with smaller discs. Figure 13.12 shows a spinning disc molecular still devised by Hickman (H28; H30). The radiant heater, the slightly bowl-shaped disc and the residue collector are seen in the front elevation, whilst the side elevation shows the assembly and the pump port.

A spinning disc still of this type has, of course, only one T.M.P. To achieve fractionation, multiple distillation with reflux is necessary.

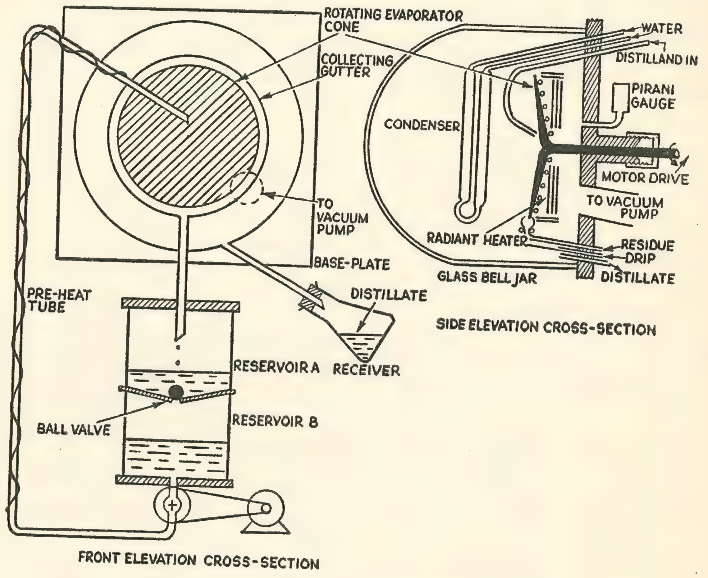

ROTATING EVAPORATOR CONE
COLLECTING GUTTER
TO VACUUM PUMP
BASE-PLATE
PRE-HEAT TUBE
DISTILLATE
RESERVOIR A
RECEIVER
BALL VALVE
RESERVOIR B
FRONT ELEVATION CROSS-SECTION
WATER
DISTILLAND IN
PIRANI GAUGE
CONDENSER
MOTOR DRIVE
TO VACUUM PUMP
RADIANT HEATER
RESIDUE
DRIP
GLASS BELL JAR
DISTILLATE
SIDE ELEVATION CROSS-SECTION

FIG. 13.12 Spinning disc molecular still (*after Hickman*)

Distilland is fed to rotating evaporator cone via pre-heat tube; it passes over cone to stationary collecting gutter whence it falls back into reservoir A. A second reservoir B, separated from A by a ball-valve, enables the distilland to be successively circulated. Either the bell-jar may serve as a condenser or a separate water-cooled condenser is included. In either case, distillate collecting inside the bell-jar passes via a tube in the base-plate to a receiver

Hickman has modified this spinning disc system by using a revolving truncated cone of about 35° solid angle, and with a bottom to top width ratio of about 1 : 1·75. By providing condensing surfaces at different heights opposite to the evaporating surface of the rotating cone, a reflux and fractionating effect is obtained. Figure 13.13 shows the principles of this still (the dimensions are arbitrary).

The distilland at 1 is fed on to the hot cone at some point up its side. From there it evaporates on to the cooled condenser, 2, and falls down to a lower part of the rotating cone where it is again evaporated on to condenser, 3, and eventually condenser, 4, from whence it is discharged on to the distillate condenser, 5. The heavier constituents of the charge climb gradually up the side of the cone and are discharged through 6 into the residue collector, 7.

Using an industrial still of this type, Hickman found that the film thickness was between 0·04 mm and 0·08 mm when the throughput was 750 kg/hr, whilst the time during which the liquid remained in contact with the hot zone was of the order of one second. The output of distilland, which had a vapour pressure of 0·05 to 0·06 torr, was 300 kg/hr. Hickman's stills have been used successfully for the production of oil-soluble vitamins.

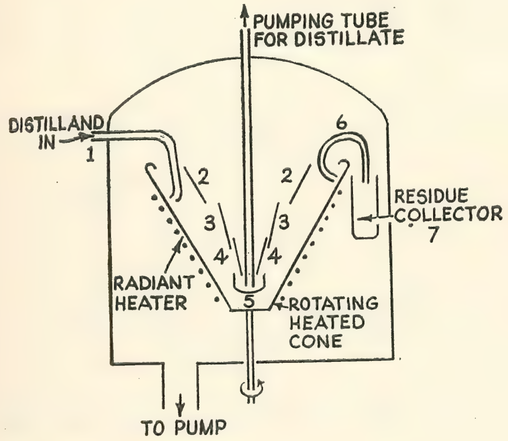

PUMPING TUBE FOR DISTILLATE
DISTILLAND IN
1
2
3
4
5
6
2
3
4
RESIDUE COLLECTOR
7
RADIANT HEATER
ROTATING HEATED CONE
TO PUMP

FIG. 13.13 Fractionating centrifugal molecular still (*after Hickman*)

The considerable technical complications of the rotary centrifugal stills have stimulated the chemical engineers in the U.S.A. and Germany to concentrate their inventive efforts upon the improvement of the falling-film still. Indeed, the trend at present seems to be in the direction of designing such stills which offer satisfactory freedom from thermal damage for the majority of substances which have to be distilled *in vacuo*, namely, plasticizers, fatty acids and chemicals from petroleum (Benner and Di Nardo, BD2; Oetjen, O4) and, possibly, in due course, the vitamin concentrates.

In this direction, an innovation is the **remote condenser falling-film still.** This does not aim at fractionating distillation and its practical separation rate is about 0·5 T.M.P. It is intended to be used for those substances which are insufficiently stable to be distilled at a pressure of 20–50 torr, but would not significantly decompose at temperatures corresponding to vapour pressures of 0·1 to 1 torr. Rates of distillation of the order of 35 lb/hr per sq ft of evaporation surface have been obtained in the preparation of di-2-ethyl hexyl sebacate [$C_8H_{16}(COOC_8H_{17})_2$], *i.e.* Octoil S, at evaporation temperatures around 175° C, vapour pressures of about 0·3 torr and residual air pressures less than 5×10^{-3} torr (BD2).

The remote condenser falling film still is illustrated by Fig. 13.14. The evaporator is a stainless steel tube 8 in. long and 8 in. dia with spiral grooves in its surface and fitted with a heater (Dowtherm was used) located on top of the water-cooled condenser. The preheated distilland entering the dome is distributed by two feed-lines (diametrically opposite one another) on to an

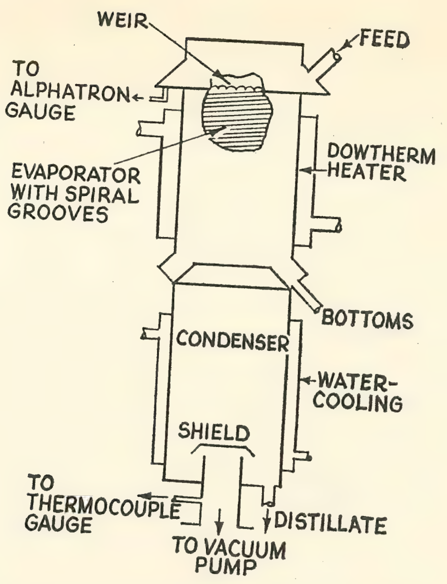

WEIR
FEED
TO ALPHATRON GAUGE
EVAPORATOR WITH SPIRAL GROOVES
DOWTHERM HEATER
BOTTOMS
CONDENSER
WATER-COOLING
SHIELD
TO THERMOCOUPLE GAUGE
DISTILLATE
TO VACUUM PUMP

FIG. 13.14 The remote condenser falling-film still

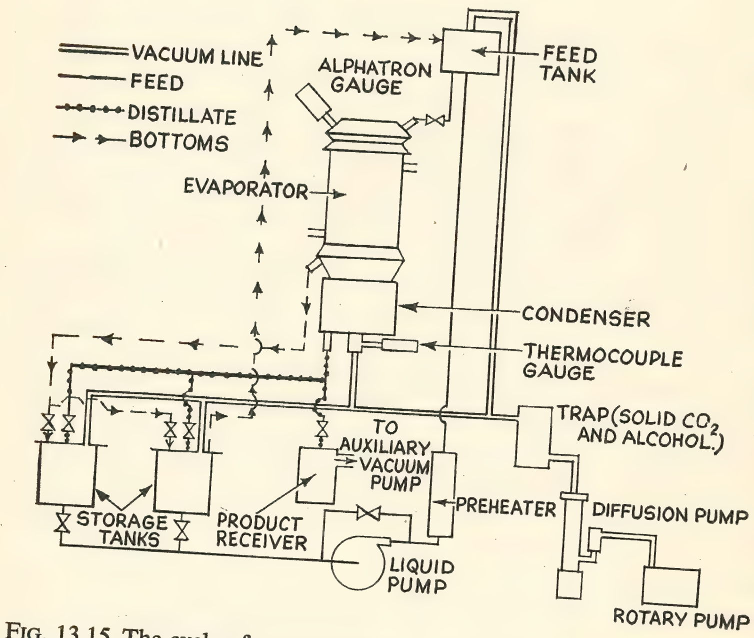

VACUUM LINE
FEED
DISTILLATE
BOTTOMS
ALPHATRON GAUGE
FEED TANK
EVAPORATOR
CONDENSER
THERMOCOUPLE GAUGE
TRAP (SOLID CO2 AND ALCOHOL)
TO AUXILIARY VACUUM PUMP
PREHEATER
DIFFUSION PUMP
STORAGE TANKS
PRODUCT RECEIVER
LIQUID PUMP
ROTARY PUMP

FIG. 13.15 The cycle of operations in a remote condenser falling-film still

overflow weir which is arranged within the inner wall of the dome. The liquid runs down the spiral grooves cut in the wall of the evaporator, its speed of flow being controlled so that the grooves are completely covered. The heated area from which evaporation takes place is about 0·9 sq ft. The temperature of the liquid film is high enough for thorough degassing—which is carried out in the film itself—but not so high as to produce boiling.

To obtain an evaporation rate of about 35 lb/hr/sq ft, the vapour pressure should be about 0·25 torr when the velocity of the vapour is about 200 ft/sec and the volume passing through the narrowest portion of the still is about 40 cu ft/sec.

Figure 13.15 illustrates the distillation cycle. The distilland in the storage tanks (1 gallon each) is first degassed by the mechanical rotary pump (displacement: 12·5 cu ft/min) and is then circulated over the evaporator. When the pressure obtained by a 2 in. diffusion pump is less than 5×10^{-3} torr, as recorded by a thermocouple gauge, heating is begun at a temperature adjusted to the desired rate of evaporation. Bottoms (the high boiling point fraction which remains behind) and distillate are returned to the storage tanks and re-cycled. The distillate can be withdrawn as soon as a constant rate of evaporation has been attained.

Pressure measurements are carried out with an Alphatron gauge, which measures the total pressure, and a thermocouple gauge, which measures the air pressures plus that of any vapour which is not held back in the condenser. Temperature measurements of the distilland and the bottoms are made by iron–constantan thermocouples inserted where needed.

The total heat traversing the evaporator at an average temperature of the liquids (feed and bottoms) of 360° F is about 9500 B.t.u./hr/sq ft, whilst the temperature of the Dowtherm vapour used in the heating jacket of the still is about 485° F. The vapour pressure of the distilland (Octoil S) under these conditions was about 0·25 torr (air pressure less than 5×10^{-3} torr).

It seems likely that the remote condenser falling-film still may play a prominent rôle in both laboratory and industry for the distillation of chemicals having molecular weights in the range from 200 to about 500 (Benner and Di Nardo, BD2; Oetjen, O4). For materials with molecular weights less than 200, distillation at rough vacua (*i.e.* not molecular pressures) or even at atmospheric pressure does not present any major problems. For materials with molecular weights in excess of 1200 the required energy for evaporation will be of the same order as the energy which breaks down the chemical bonds, so chemical decomposition will occur.

Fractionating high vacuum stills, *e.g.* that of Bowman (Benner, Di Nardo and Tobin, BDT1) (National Research Corporation) having up to 18 T.M.P. are in the laboratory stage of development. A number of problems of design and control have yet to be solved; they are under serious consideration.

14

VACUUM METALLURGY

14.1. Introduction

In the production and processing of metals the main advantages attendant upon heating the metal or other material, such as an inorganic compound of the metal with a reducing agent, in vacuum as compared with conventional procedures are:

(1) The heated or molten metal is protected from reaction with the gases in the atmosphere.

(2) The metal can be distilled or sublimed with a much faster effective rate of evaporation at a reduced operating temperature.

(3) The heated metal in vacuum releases dissolved gases leading to marked improvements in mechanical and electrical properties.

(4) Degassing and deoxidation with the help of carbon is more effective as the carbon reacts with oxides more readily as the surrounding gas pressure is reduced.

(5) In a metallurgical process in which gas or metallic vapours are evolved, the reaction is more rapid and more complete.

(6) A greater control is possible over the production of certain valuable alloys where the percentages of the constituents must be kept within defined limits from one batch to another.

These advantages have facilitated the metallurgy of highly reactive metals and alloys and have also led to the supply of such metals as copper, steel and especially high temperature steel alloys with low gas content and much reduced occlusions of small quantities of undesirable metallic and other impurities. The demand for special metals and alloys in the aircraft industry, particularly for jet engines, for the construction of nuclear reactors and nuclear power plants and, now, for guided missiles, has led to the use of vacuum in the processing of metals some of which were formerly virtually confined to the research laboratory or used only in the electron tube industry. Examples are beryllium, columbium, magnesium, molybdenum, tantalum, thorium, titanium, tungsten, uranium, vanadium and zirconium. Up to 1950, vacuum metallurgy was rarely concerned with melts exceeding 300 lb in weight; subsequently, the processing of tonnage melts has developed in industry.

The development of large-scale vacuum metallurgical plants has attended and, indeed, made more urgent the provision of high speed vacuum pumps to remove the enormous quantities of gas which are evolved from large masses of heated metal in the vacuum furnace. Accompanying requirements

are large argon-arc welded steel alloy vacuum tanks, suitable means of heating the metal in vacuum, the provision of satisfactory demountable seals, ceramic insulators, isolation valves, rotatable tilting and stirring devices, vacuum gauges and leak detection facilities.

The chief procedures which are undertaken in vacuum metallurgy are:

(1) Heating of the metal in the solid state to cause degassing and/or annealing, cleaning or ageing and to perform brazing. Such processes are known collectively as **vacuum heat treatment.**

(2) Degassing of the molten metal in a ladle or by the stream degassing method, both of which have been applied to the degassing of steel on a very large scale.

(3) Melting of the metal which may then be cast into a mould in vacuum and where, furthermore, the addition to the melt of alloying constituents or of a deoxidizing agent like carbon is practised.

(4) Fusion of the metal in an arc which is struck either in the residual gas (which includes vapour of the metal) or in an inert gas.

(5) Distillation or sublimation of the metal and particularly distillation to purify metals.

(6) Sintering: highly refractory metals like tantalum, titanium, columbium and compounds like carbide tool material are sintered in vacuum from compressed powder shapes at high temperature.

(7) In some cases, extraction of the metal from an inorganic compound by a thermal reduction process. Here usually only one or two stages in the complete processing schedule are carried out in vacuum.

14.2. Methods of Heating Employed

To carry out the heating of the metal (and, in some cases, non-conducting materials) in a vacuum furnace, techniques employed are:

(1) **Electrical resistance heating.** Three procedures are:

(*a*) The material is contained within an evacuated tube or retort which is heated externally by current passing through, for example, nickel–chrome heater elements which are in air. These retorts are usually of silica in smaller sizes and stainless steel or high nickel alloy in the larger sizes. In these cases, also, gas heating and sometimes oil heating are used.

(*b*) The metal or other material is placed in a crucible around which is wound the heater spiral which carries electric current. The crucible is usually of re-crystallized alumina or a mixture of zirconium and thorium oxides or magnesium and thorium oxides and is mounted, with the heater elements, within the vacuum chamber. The heater spiral is of molybdenum, tantalum or tungsten.

(*c*) In the vacuum chamber, the crucible containing the charge or, alternatively, a shape made of the pressed metal or other material is heated by radiation from an electric heater in the form of tungsten or molybdenum spirals or rods or graphite rods.

Furnaces of type (*a*) are known as **vacuum retort furnaces**; those of types (*b*) and (*c*) are called **vacuum resistance furnaces**. In the latter, to conserve heat and improve the efficiency of electrical heating, radiation shields disposed around the crucible and heater elements are used.

(2) **Induction heating** in which (*a*) the charge is heated by eddy currents induced directly into it from a coil carrying high-frequency a.c. around the crucible and where (*i*) the crucible is in vacuum and the coil is in air or (*ii*) both the crucible and the coil are in vacuum; (*b*) the metal or other material is heated through an intermediate susceptor. Here, **vacuum induction furnaces** are concerned.

(3) **By the use of an arc discharge.** In the **vacuum arc furnace** the ingot is usually formed in a water-cooled crucible beneath an adjustable electrode with the arc voltage supply between the crucible and this electrode. The electrode may be of tungsten or a tungsten-tipped rod or of graphite; alternatively, this electrode is pre-formed or continuously formed from the metal to be melted. The latter is the consumable electrode or **consutrode** method. The arc discharge is set up in an inert gas filling (*e.g.* of neon) if a tungsten, tungsten-tipped or graphite electrode is used, but is set up in the residual gases and vapours in the evacuated furnace or in inert gas for the consutrode method.

Other heating procedures less commonly employed are electron bombardment (Smith, Hunt and Hanks, SHH1; Candidus and Simons, CS1; *see also* § 10.3) and levitation melting (§ 10.3).

For many degassing, melting and sintering operations in vacuum it is important to choose between electrical resistance heating and induction heating and also to decide between the various methods of applying electrical resistance heating. Arc discharge methods are used chiefly for highly refractory metals like molybdenum and columbium.

Resistance furnaces in which the crucible with wound-on heater is in vacuum can be used at temperatures up to 1700° C. By the use of molybdenum radiation heaters and shields, resistance furnaces for operation up to 1800° to 2000° C can be constructed or up to 2500° C if graphite heater rods and radiation shields are used. The vacuum retort furnace with external heating is limited to a maximum temperature of about 1200° C.

Induction heating is carried out by passing a.c. through a coil around the crucible of a frequency decided primarily by the mass of the metal in the crucible. For the melting of steel, Moore (M21) recommends:

up to 30 lb:	10,000 c/s
30 to 1000 lb:	3000 c/s
over 1000 lb:	960 c/s

To provide large power at such frequencies, a motor generator set (rotary converter) is required, but valve oscillators are used for low power.

The use of an internal electrical heat source in vacuum gives rise to difficulties with corona discharge at voltages above 100 V, and particularly above 400 V, when the residual pressure of the gases and vapours is in the range from about 3×10^{-2} to 3 torr. Consequently, it is necessary to limit the potential difference across the coil to about 400 V maximum. The coil current demands are therefore very high for the vacuum processing of large masses of metal, as the power requirements may reach several hundred kilowatts. This limitation applies to both resistance and induction heating and, furthermore, in the case of the latter, it means that too high a frequency of the a.c. is prohibited because the peak p.d. across the coil is largely decided by $2\pi fLI$ where f is the frequency, L the coil inductance and I the peak current, assuming the coil resistance is negligible compared with its reactance.

In choosing between electrical resistance heating and induction heating the following factors are important:

(*i*) To supply the a.c. at mains frequency for resistance heating only a step-down transformer is required with a means of varying the primary voltage from the mains; for induction heating in large plants an expensive motor generator set together with electrical control equipment is necessary. Roughly, the costs of resistance heating are one half that of induction heating for the same power.

(*ii*) Whereas resistance heating is used often at temperatures up to 1200° C, the larger vacuum furnaces for temperatures of 1000° to 2000° C—and especially those for melting metals—are usually of the induction-heated type. Though the resistance heating method with radiation heater elements and shields enables higher temperatures to be attained, it is difficult to construct a freely suspended heater element with a minimum of refractory support (with which it may react) and yet able to withstand the stresses involved in operation. Moreover, the use of radiation heating demands careful consideration of the work configuration to ensure efficient heat transfer by radiation and uniformity of temperature. These problems are particularly difficult to solve where large masses of metal are to be melted.

(*iii*) The induction-heating method is less efficient in that considerable losses occur as the power factor with respect to the coil is low (Kramers and Dennard, KD1).

(*iv*) The induction coil itself is not heated significantly (indeed, it may be water-cooled) by the current through it, as the heating effect is due to eddy-currents set up in the charge itself. The refractory of which the crucible is made need not therefore be heated above the temperature of the charge and hence the crucible life is longer; in resistance heating, the coil and crucible exterior in contact with the coil are necessarily heated to a higher temperature than the charge.

(*v*) Induction heating with a water-cooled coil enables more rapid temperature changes in the charge to be produced, and the charge can be cooled more quickly.

(*vi*) The use of a motor generator to provide a.c. for induction heating permits the power input to the crucible and its charge to be smoothly regulated.

(*vii*) Induction heating causes stirring of the molten metal in the crucible.

Vigorous stirring of the melt is most important, especially when alloying constituents or deoxidizers are added, and to ensure quicker outgassing because gas is evolved readily at the melt-vacuum interface.

Such eddy movements of a melt are greater, the greater the power supplied to a given charge and the lower the frequency of the induced a.c.

Data of use in calculations on resistance heating and induction heating are given in Appendix B.

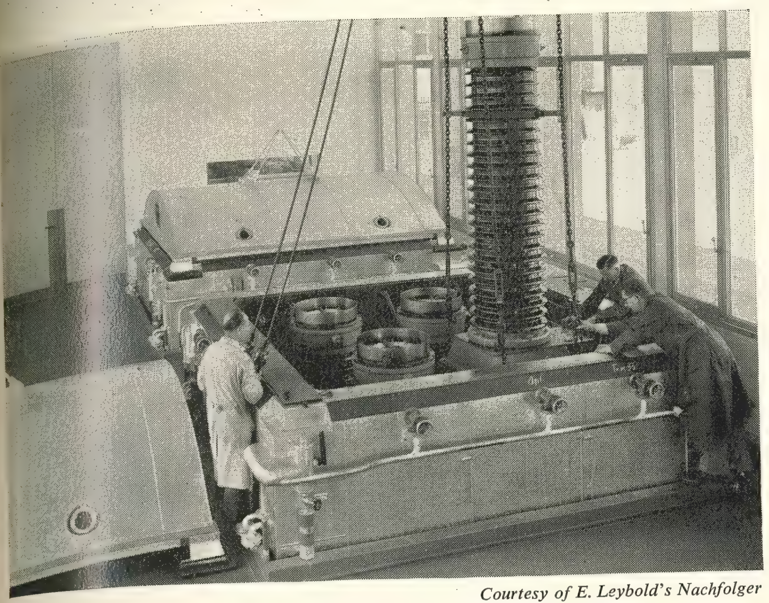
Types of Vacuum Furnace

A large number of vacuum furnaces of a wide range of sizes and applications have been described in the literature. In several cases it is essential to consider the design of the furnace in relation to the particular vacuum metallurgical operation concerned. However, much common ground exists between the various designs, so in the following sections typical models are considered with preliminary remarks about their uses. Further details of some of the basic processes in vacuum metallurgy are considered later.

14.3. Vacuum Retort Furnaces for Heat Treatment

As mentioned in § 14.2, these have the heater element in air outside the evacuated retort; the retort hence serves both as the vacuum chamber and as the crucible containing the solid material to be treated. The use of such furnaces for the small-scale degassing of metal parts for electron tube assemblies has already been considered in a preliminary way in § 6.4. The furnaces commonly have a retort made of fused silica or nickel–chrome (80% Ni; 20% Cr) (*see* Fig. 6.1) and are evacuated to a pressure of 10^{-3} torr or less by a two-stage gas-ballast pump or such a pump backing a diffusion pump. The heating time for a medium size furnace (say, 24 in. long and 6 in. dia) is usually 6 to 8 hours at the maximum temperature with a total processing time (heating up and cooling) of 12 to 24 hours. The maximum temperature is chiefly limited by the lifetime of the heating element (Espe, E10). This temperature is 1000° C for a Nichrome element (80% Ni; 20% Cr) and 1200° C for Kanthal (20 to 30% Cr; 5% Al; rest Fe). Though a temperature of 1000° to 1200° C is adequate for the degassing from the solid state of most metals, molybdenum, tantalum, tungsten and also graphite demand higher temperatures whereas copper and certain copper alloys need a lower temperature of 500° to 550° C. For temperatures of about 1500° C, Espe recommends a retort of sintered alumina heated by a molybdenum winding. To prevent oxidation of this molybdenum, the evacuated retort is placed within a metal tube and the space between this retort and the outer envelope is filled with hydrogen or a mixture of hydrogen and nitrogen. Vacuum furnaces for yet higher temperatures are, however, of the type described in § 14.4 with the tungsten or molybdenum heater element within the vacuum chamber, or employ induction heating.

Figure 14.1 shows two types of vacuum retort furnace for the degassing of metal parts (Espe, E10): (*a*) is a two-zone horizontal furnace; (*b*) is a double vertical furnace arrangement. A convenient alternative to (*a*) which permits



Courtesy of E. Leybold's Nachfolger

Plate 11

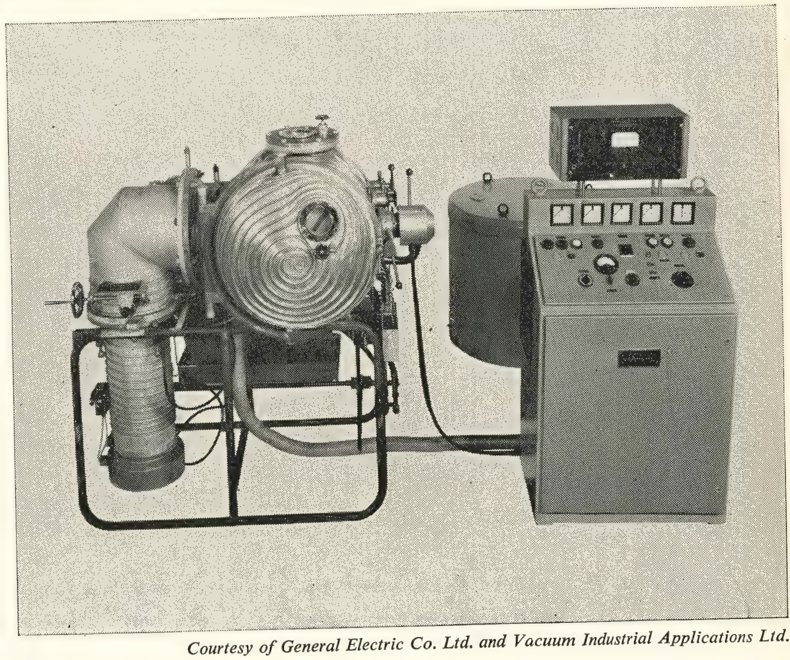
A high vacuum impregnating tank of capacity 33 m^3 is being charged with high voltage measuring transformers at Siemens, Berlin (*see* p. 438).

Plate 12

A general-purpose vacuum furnace

Both resistance and induction heating are provided. With the former, temperatures of 1200 to 1400° C can be achieved with a refractory crucible and 1800° C if a graphite crucible is used. Induction heating permits much faster heating rates and a maximum temperature limited only by the crucible material.

The furnace chamber is of steel with an inner surface of stainless steel. It has an internal diameter of 24 in. and has a 10 in. bore side tube to the oil diffusion pump (speed: 2000 litres per sec at 10^{-3} torr; backed by a rotary pump of displacement 1300 litres per min.). For melting metals, three charge-carrying containers are fitted internally and also a feed chute, thermocouple and crucible cover. The resistance and induction heating units are interchangeable; the induction heating current is at a frequency of 3–10 kc/s. Resistance heating is at 20 kW max and requires 3·5 gal per min of cooling water. Induction heating is rated at 17 kW and the water flow requirement is the same. Operations possible are melting and casting, degassing and sintering (*see* p. 478).

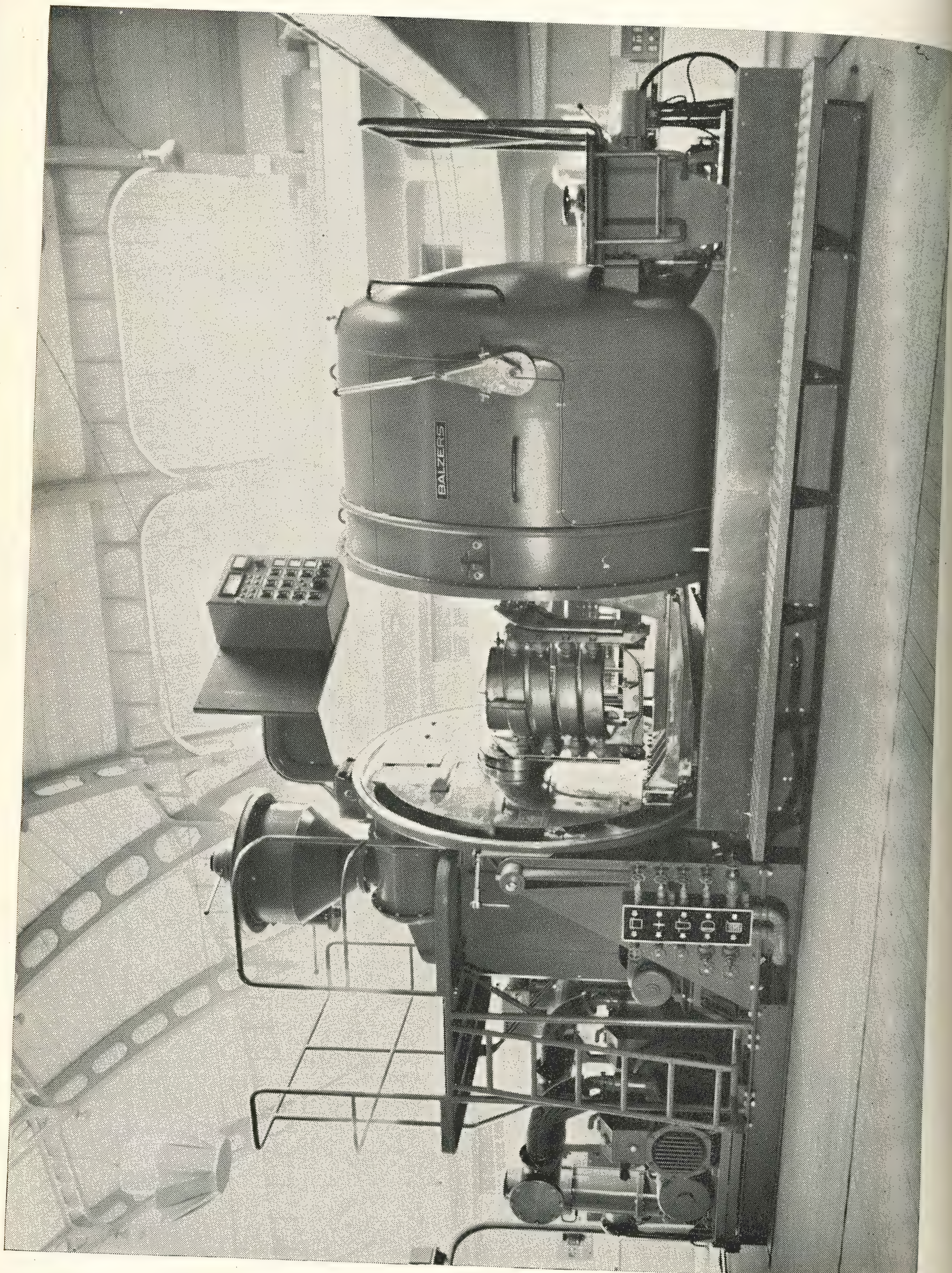


Courtesy of General Electric Co. Ltd. and Vacuum Industrial Applications Ltd.

Plate 13

A large vacuum induction furnace for the melting and casting of metals

Crucible volume: 30 litres; speed of pump: 8000 litres per sec; ultimate vacuum: 10^{-5} torr (*see* p. 483).



Courtesy of Geraetebau-Anstalt Balzers

rapid cooling is the dolly type furnace (Fig. 14.1(*c*)) such as that made by Geraetebau-Anstalt Balzers: the charge is in a horizontal evacuated cylindrical tube mounted on a trolley together with the vacuum pumps, so that it can be moved into and out of the stationary furnace proper; withdrawal of the tube from the furnace facilitates cooling.

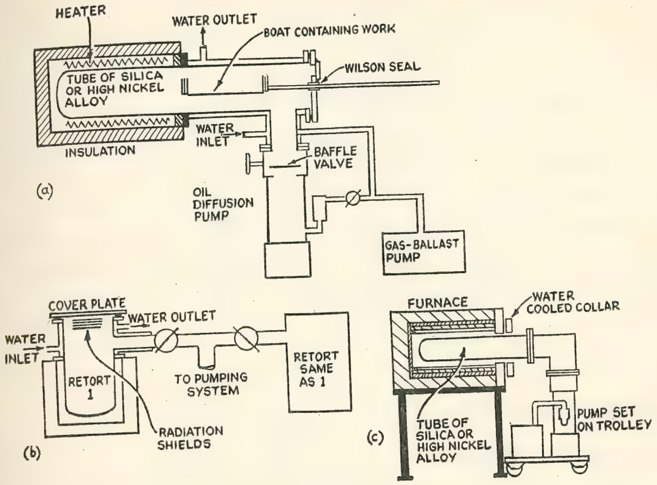

HEATER
WATER OUTLET
BOAT CONTAINING WORK
WILSON SEAL
TUBE OF SILICA OR HIGH NICKEL ALLOY
WATER INLET
INSULATION
BAFFLE VALVE
(a)
OIL DIFFUSION PUMP
GAS-BALLAST PUMP
COVER PLATE
WATER OUTLET
WATER INLET
RETORT 1
TO PUMPING SYSTEM
RETORT SAME AS 1
RADIATION SHIELDS
(b)
FURNACE
WATER COOLED COLLAR
TUBE OF SILICA OR HIGH NICKEL ALLOY
PUMP SET ON TROLLEY
(c)

FIG. 14.1

(*a*) A two-zone vacuum retort furnace
(*b*) A double vacuum retort furnace
(*c*) A dolly type vacuum retort furnace

Large vacuum retort furnaces are usually fabricated from high nickel alloy; they are costly and the maximum permissible temperature is 1200° C. Furthermore, a large metal retort at high temperature with the heater element outside it in the atmosphere, is liable to mechanical deformation due both to its weight and to the pressure of the atmosphere. To minimize the former, a vertical rather than a horizontal tube retort is used; to prevent the effects of atmospheric stress, the whole evacuated retort may be surrounded by a

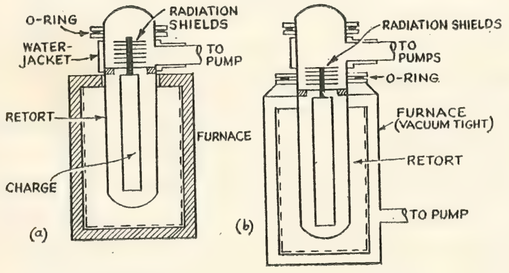

O-RING
RADIATION SHIELDS
WATER-JACKET
TO PUMP
RETORT
FURNACE
CHARGE
(a)
(b)
RADIATION SHIELDS
TO PUMPS
O-RING
FURNACE (VACUUM TIGHT)
RETORT
TO PUMP

FIG. 14.2

(*a*) A single-pumped pit type vacuum retort furnace
(*b*) A double-pumped version (*after Giler*)

second, water-cooled vessel which is roughed out by a separate pump to a pressure of about 1 torr, leading to a double-pumped arrangement; the heated retort is then negligibly stressed whilst the outer vessel is at room temperature and readily able to withstand the atmospheric pressure.

Giler (G23) illustrates two pit-type vacuum furnaces. The first (Fig. 14.2(*a*)) is single-pumped, the second (Fig. 14.2(*b*)) is double-pumped.

Furnaces of this type as much as 20 ft in height have been constructed. The large thermal capacity of these big furnaces makes them difficult to cool. Cooling is speeded up by admitting inert gas to the retort after the heat treatment is completed; for a double-pumped furnace, air is simultaneously admitted to the space between the retort and the outer shell. In pit furnaces, a cooling chamber is often attached to the top of the retort and the charge raised into it by a winch. A series of cooling chambers separated by large gate valves is also possible (Giler, G23).

14.4. Vacuum Resistance Furnaces

Vacuum resistance furnaces have the heating element within the evacuated chamber either immediately around the crucible so that the heat is conveyed from the element through the crucible walls to the charge inside or this element is arranged to heat the charge by radiation. The former set-up is frequently used for vacuum melting, especially in small scale plant and, as such, is a rival of induction heating, so will be considered in § 14.5. Radiation heating is much practised in small vacuum furnaces for the heat treatment at high temperatures of metals and for sintering.

Several models of vacuum resistance furnaces employing radiation heating elements and radiation shields have been developed. An excellent design is that due to Kramers and Dennard (KD1). These authors point out that resistance heated furnaces with the molybdenum or tungsten wire in close contact with a refractory support suffer from the disadvantage that gaseous products result from the chemical reaction between the element and the refractory, especially when attempting to attain temperatures exceeding 1500° C. The ideal is therefore a freely suspended heater element, which has been virtually achieved in the design put forward (Fig. 14.3(*a*)). This is erected within a water-cooled steel chamber (dia: 18 in.; height: 30 in.) exhausted by an oil diffusion pump of speed 300 litre/sec with a mechanical backing pump of displacement 224 litre/min. The heater element consists of a series of 10 horizontal strips of molybdenum (each 22 cm × 0·5 cm × 0·0275 cm) welded to the main molybdenum connectors through tantalum inserts (0·1 mm thick). Cross-member supports are provided at equipotential regions of the heater (Fig. 14.3(*b*)). Surrounding this heater there are five coaxial cylindrical molybdenum radiation shields and a series of molybdenum baffle plates are mounted above and below the hot zone. The main molybdenum current leads (1·25 in. wide; 0·035 in. thick) to the heater are bolted to a radiation screen at about 3 cm from each end of the hot zone; insulation is provided by

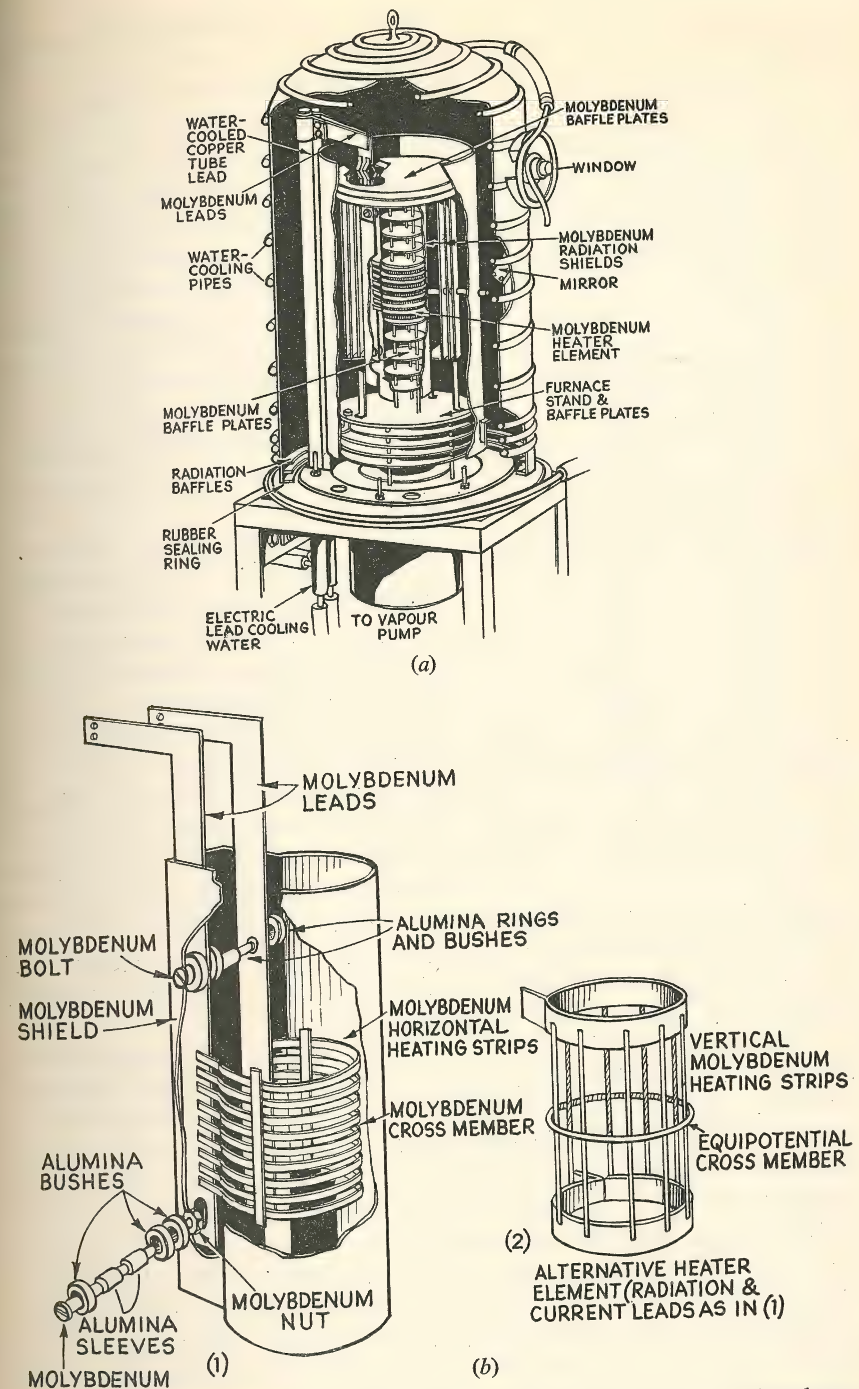

WATER-COOLED COPPER TUBE LEAD
MOLYBDENUM LEADS
WATER-COOLING PIPES
MOLYBDENUM BAFFLE PLATES
RADIATION BAFFLES
RUBBER SEALING RING
ELECTRIC LEAD COOLING WATER
TO VAPOUR PUMP
MOLYBDENUM BAFFLE PLATES
WINDOW
MOLYBDENUM RADIATION SHIELDS
MIRROR
MOLYBDENUM HEATER ELEMENT
FURNACE STAND & BAFFLE PLATES
(a)
MOLYBDENUM LEADS
ALUMINA RINGS AND BUSHES
MOLYBDENUM BOLT
MOLYBDENUM SHIELD
MOLYBDENUM HORIZONTAL HEATING STRIPS
MOLYBDENUM CROSS MEMBER
ALUMINA BUSHES
ALUMINA SLEEVES
MOLYBDENUM
MOLYBDENUM NUT
(1)
VERTICAL MOLYBDENUM HEATING STRIPS
EQUIPOTENTIAL CROSS MEMBER
(2)
ALTERNATIVE HEATER ELEMENT (RADIATION & CURRENT LEADS AS IN (1)
(b)

FIG. 14.3 A vacuum resistance furnace with molybdenum radiation heating element

(*a*) Vacuum furnace (*after Kramers and Dennard*)
(*b*) Heater assemblies for a vacuum resistance furnace

recrystallized alumina. To allow differential expansion with the outer shield, the lower current lead bolt is not tight and the lead itself is slotted.

The effective hot zone within the molybdenum heater is 5 in. high by 3 in. dia and 10 kW is dissipated in the heater. The supply is from a step-down transformer furnishing 10 V at 1000 amp to the heater element. This furnace can be operated for long periods at temperatures up to 1800° C though at 2000° C difficulty arises due to softening of the molybdenum, likely to cause short circuiting. This distortion is particularly likely in the main current leads and is probably aggravated by the magnetic force between these leads. Operation is successful in a vacuum (minimum pressure: 10^{-5} torr) or with a hydrogen filling at a pressure below 5 torr. Applications of this furnace have been chiefly to the preparation and sintering of ceramic powders and metal-ceramic mixtures.

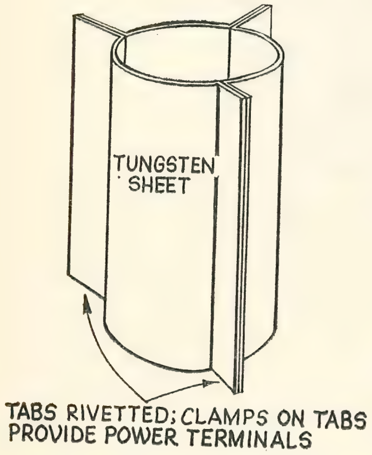


FIG. 14.4 A sheet-type heating element

Sibley (S30) describes a vacuum resistance furnace to attain temperatures of 2200° C made at the National Research Corporation in which radiation heating is used from a heater element in the form of sheets of tungsten made into a cylinder. The maximum temperature possible with tungsten is stated to be 2600° C, for tantalum, 2400° C and for molybdenum, 1800° C. The single sheet construction for a heater is attractively simple though Kramers and Dennard (KD1) allege that it gives a less robust construction than their use of strips. The warpage with tantalum and molybdenum is more severe than with tungsten (Sibley, S30) so a greater heater to radiation shield spacing is demanded. Tungsten becomes very brittle after heating in vacuum.

The furnace described by Sibley has a water-jacketed stainless steel vacuum chamber. The vertical heater assembly is made from three sheets of tungsten (0·015 in. thick) which are shaped to form a cylinder with vertical tabs at spacings of 120° around the outside (Fig. 14.4); the sheets are rigidly fastened at these tabs by tungsten rivets. Water-cooled clamps to the tabs provide power terminals and also rigid support for the heater. This arrangement is convenient for three-phase delta connection to the a.c. supply. Around the heater are mounted four tungsten and two molybdenum radiation shields in the form of coaxial cylinders; these are supported and spaced by tungsten pins and washers. The effective hot chamber within the heater has a height of 10 in. and a diameter of 5 in. The voltage supply is 10 V to obtain 2400° C. The cooling rate is usefully high: from 2400° to 400° C in 15 min at a pressure of 10^{-5} torr. The pumping system consists of an oil diffusion pump with a speed of nearly 600 litre/sec at 10^{-4} torr backed by a mechanical pump with

a displacement of 840 litre/min and a holding pump of displacement 56 litre/min.

This furnace was developed for the vacuum heat treatment of reactive metals (*e.g.* tantalum) and ceramics at temperatures from 2200° to 2500° C.

The use of carbon rod and strip heaters has been explored for high temperature vacuum furnaces but the vapour pressure of carbon at 2400° C is about 10^{-3} torr compared with that of tungsten at 2×10^{-7} torr (Dushman, D1). Giler (G23) illustrates a vacuum furnace with a heating element made from a single piece of graphite and with graphite radiation shields. This is intended for operation at 2200° C, where the vapour pressure of carbon is about 2×10^{-7} torr.

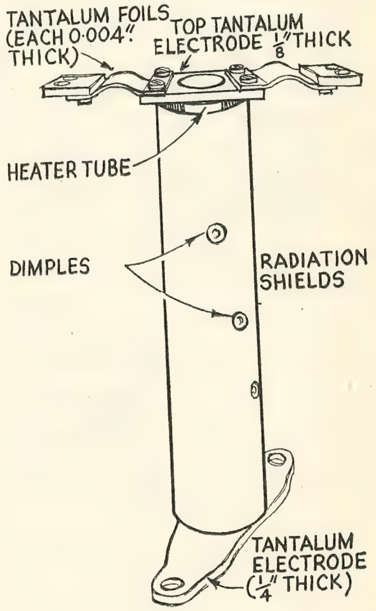

TANTALUM FOILS (EACH 0·004" THICK)
TOP TANTALUM ELECTRODE 1/8" THICK
HEATER TUBE
DIMPLES
RADIATION SHIELDS
TANTALUM ELECTRODE (1/4" THICK)

FIG. 14.5 A tantalum or tungsten heater tube assembly (*after Dickinson*)

Dickinson (D15) has described a vacuum resistance furnace capable of running at 2500° C for days and able to attain 3000° C. The heater is a tube of tantalum for the lower temperature and of tungsten for the higher. In both cases, the electrodes and radiation shields are made of tantalum. Dimples in the coaxial, cylindrical radiation shields provide definite regions of support and so reduce the possibility of them adhering together indiscriminately by direct contact at high temperature. The bottom tantalum electrode ($\frac{1}{4}$ in. thick) supports the heater tube, whilst the top electrode is constructed of $\frac{1}{8}$ in. thick tantalum plate with flexible sections made from sheet 0·004 in. thick (Fig. 14.5). The tantalum heater tubes used are 10 in. long, 1 in. dia and 0·02 in. wall thickness and proved satisfactory up to 2500° C. For 3000° C, rolled split tungsten tubing with a wall thickness of 0·030 in. is employed (available from Metallwerke Plansee Corporation, Austria). Power is obtained from a 45 kVA transformer with the secondary tapped at 5, 10, 15, 25 and 50 V and the primary voltage (max: 440 V) adjustable by a motor-driven variac. The possibility of using rhenium in place of tantalum to permit the furnace to be run in a hydrogen atmosphere (tantalum inadmissible owing to gas sorption) is mentioned.

The vacuum chamber (water-cooled copper tube; dia: 9 in.) is evacuated by an oil diffusion pump (speed: 300 litre/sec) with a liquid nitrogen trap. Pre-heating at 1200° C for several minutes reduces the otherwise severe subsequent outgassing at high temperatures. At 2000° C, a pressure of 10^{-5} torr could be maintained in the furnace; at 2500° C, 3×10^{-5} torr and at 3000° C, 10^{-4} torr.

14.5. Vacuum Resistance and Induction Furnaces for Melting and Casting Metals

In general, vacuum furnaces for melting metals are resistance or induction heated for small scale work and induction heated for large scale. Some furnaces have provision for either method of heating. In vacuum melting furnaces, the metal or other material is melted in a crucible, alloying and other constituents may be added, and the melt is often poured (cast) into a mould within the vacuum. Irrespective of the heating method, certain common features of the furnace designs may be noted.

The vacuum chamber is water-cooled, has a surface area of about 1000 cm^2 per kilowatt of energy supplied (Malcolm, M22), and is made of non-magnetic stainless steel if induction heating is used to reduce induction losses. Tanks for resistance heated vacuum furnaces may alternatively be made of mild steel with the inner surface electroplated (with nickel or chromium) or coated with stainless steel or enamelled. The tank should have a polished interior to facilitate cleaning.

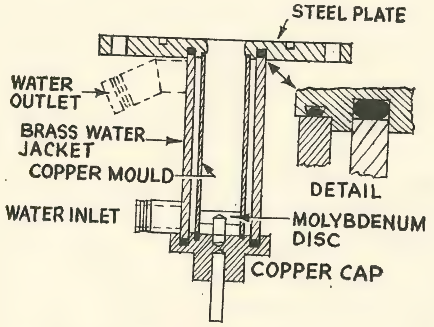


FIG. 14.6 A water-cooled copper mould

The pumping system must be able to handle large gas throughputs at pressures in the region of 10^{-4} to 10^{-1} torr. Small and medium size plants usually employ a diffusion-ejector pump backed by a gas-ballast rotary pump. For large plants, a diffusion pump backed by an ejector pump and a gas-ballast mechanical rotary pump is usual, though Roots pumps are often used in place of an ejector or as an intermediary between a diffusion-ejector pump and the mechanical rotary pump.

The crucible in which the metal or other material is melted is made of a refractory ceramic such as recrystallized alumina, beryllium oxide, magnesium oxide, zirconium oxide, thorium oxide or, in some cases, graphite. Espe (E10) gives the maximum possible operating temperatures for these materials as MgO, 1600° C; BeO, 2100° C; ZrO$_2$, 2300° C; ThO$_2$, 2300° C; C, 2300° C. For a molybdenum heater winding, zirconium oxide is the best choice from the point of view of stability against chemical reaction; for tungsten, thorium oxide is preferred. The mould into which the molten metal is cast is often water-cooled and made of copper (Fig. 14.6), iron or steel; uncooled ceramic and graphite moulds are also used, but sand moulds are inadmissible owing to outgassing difficulties.

To pour the molten metal from the crucible into the mould in vacuum either bottom pouring or a tilting crucible or a tilting vacuum furnace is used. Bottom pouring is undertaken by one of three methods illustrated by Fig. 14.7. In Fig. 14.7(*a*) is shown the method whereby a stopper rod is lifted by a cam (operated by a mechanism connected via a rotary seal to a lever outside the vacuum chamber) to open the orifice in the base of the crucible when it is required to pour the molten metal into the mould; an alternative arrangement is to use a stopper which is rotated out of the way (Fig. 14.7(*b*)), whilst a third possibility is to use a fusable plug in the aperture in the crucible base which is melted by an auxiliary heater to begin pouring. This last method obviates the need for a movable mechanism but is liable to cause contamination of the charge.

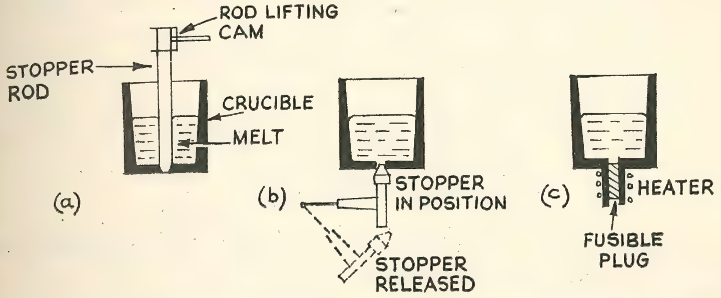


FIG. 14.7 Arrangements of bottom pouring crucibles

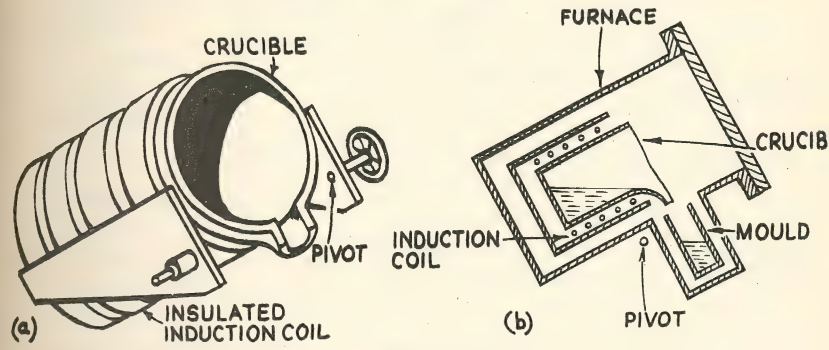


FIG. 14.8

(*a*) Arrangement of tilting crucible

(*b*) The tilting vacuum furnace method

The tilting crucible is illustrated schematically by Fig. 14.8(*a*). The crucible, provided with a suitable lip for guiding the molten charge, is tilted by the rotation of a shaft connected via a rotary seal to outside the vacuum chamber, whilst the mould is kept stationary. The alternative is to tilt the furnace itself (Fig. 14.8(*b*)), in which case the mould within it is often kept in the vertical position by arranging it to be suspended freely from a pivot.

Typical of a small vacuum resistance furnace for melting and casting metals is the Edwards High Vacuum Ltd. plant which has a crucible capacity of 100 ml (equivalent to $\frac{1}{2}$ lb of steel) (Fig. 14.9). The vacuum chamber (height: 21 in.; dia: 12 in.) is of electroplated mild steel and is pumped by an oil diffusion pump of speed 350 to 450 litre/sec at 10^{-4} torr backed by a mechanical rotary pump with a displacement of 150 litre/min. The pressure in the chamber before heating the charge is 10^{-3} to 10^{-4} torr. The pumping aperture at the base of the chamber is covered with gauze to prevent metallic particles from entering the pump.

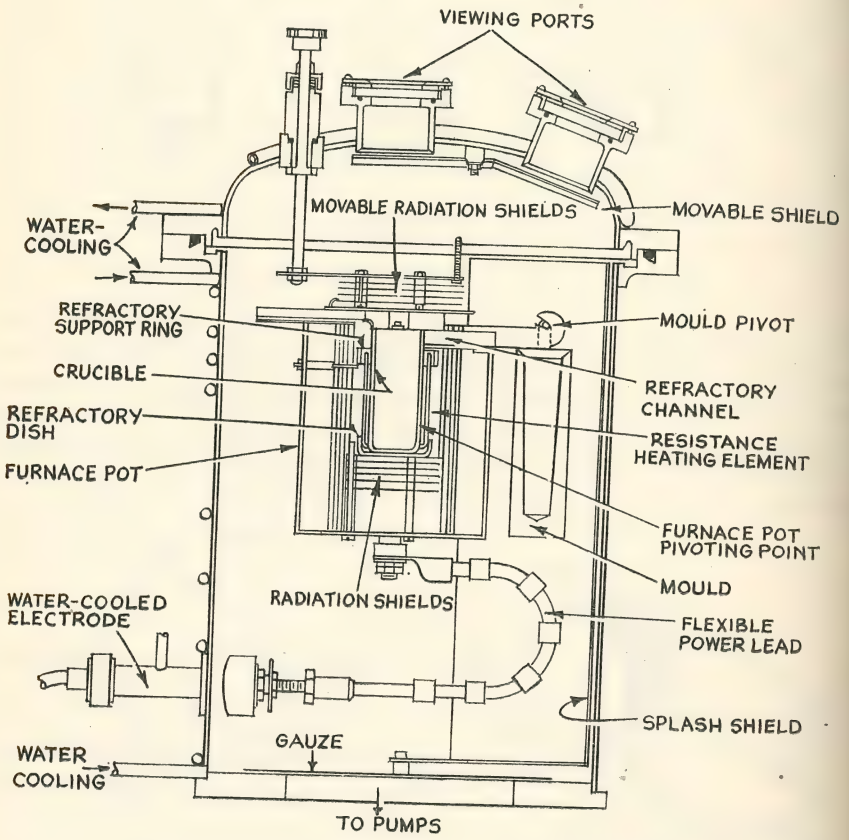

VIEWING PORTS
WATER-COOLING
MOVABLE RADIATION SHIELDS
MOVABLE SHIELD
REFRACTORY SUPPORT RING
MOULD PIVOT
CRUCIBLE
REFRACTORY CHANNEL
REFRACTORY DISH
RESISTANCE HEATING ELEMENT
FURNACE POT
FURNACE POT PIVOTING POINT
MOULD
WATER-COOLED ELECTRODE
RADIATION SHIELDS
FLEXIBLE POWER LEAD
SPLASH SHIELD
GAUZE
WATER COOLING
TO PUMPS

FIG. 14.9 Small vacuum resistance furnace for melting (*Edwards High Vacuum Ltd.*)

The refractory crucible is mounted on the axis of a furnace pot within the vacuum chamber. This furnace pot can be tilted up to 100° from the vertical by connection to an external lever via a rotary seal to enable metal melted in the crucible to be poured into the mould. The crucible stands on a dish of recrystallized alumina which supports the resistance heating element; the top of this element is held in position by a refractory ring. Radiation shields are disposed between the crucible and the furnace pot, beneath the alumina dish and above the furnace pot; this last set of shields can be swung out of the way by rotation of a vacuum-sealed shaft entering the chamber. Flexible current leads connect the heater element to water-cooled vacuum-sealed electrodes in the lower part of the chamber wall. The mould hangs freely from two hooks so that it remains vertical as the furnace pot and crucible are tilted for pouring. Sight windows are provided to enable temperature measurements on the crucible charge to be made by an optical pyrometer and to enable the casting operation to be watched. Pressure measurement is by a combined Penning and Pirani type gauge. The power unit transformer secondary for supplying the furnace heating element provides 25 V at 90 amp, the maximum power being 2·25 kVA.

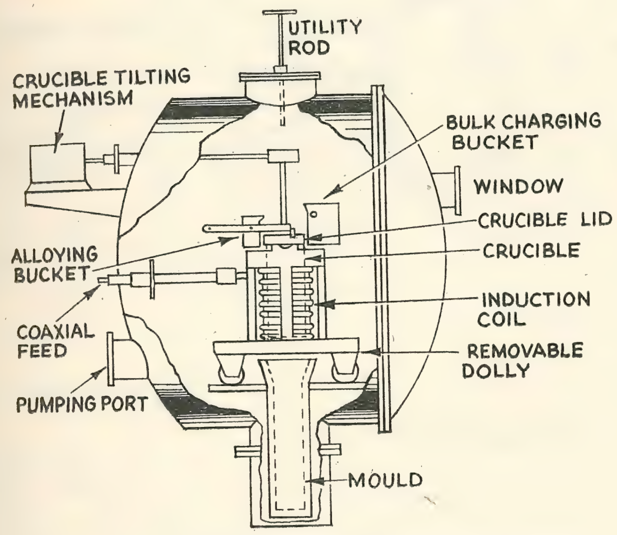

UTILITY ROD
CRUCIBLE TILTING MECHANISM
BULK CHARGING BUCKET
WINDOW
CRUCIBLE LID
CRUCIBLE
ALLOYING BUCKET
INDUCTION COIL
COAXIAL FEED
REMOVABLE DOLLY
PUMPING PORT
MOULD

FIG. 14.10 A batch type vacuum induction furnace

Sintering, melting and casting of metals in vacuum at temperatures up to 1700° C can be carried out in this plant.

The essential features of a vacuum induction furnace of the batch type (for semi-continuous furnaces, *see* § 14.6) are illustrated by Fig. 14.10, based on a diagram given by Moore (M21). The refractory crucible containing its charge can be wheeled into position in the open furnace (with a horizontal cylindrical tank the vertical cover lid is removed; this is usually sealed by a Neoprene O-ring and clamped). The induction coil around the crucible is supplied with a.c. at audiofrequency via a coaxial feed, preferred to the use of draped flexible leads because the latter are more liable to leakage, have higher inductive losses and are more difficult to construct for large current loads. The furnace shown is of the bottom-pouring type with the mould below the crucible. Further provisions are a cover lid for the crucible (the radiation loss from the melt and the top of the crucible may increase by 250% if this cover lid is removed), a bucket for bulk charging of the crucible, a smaller bucket or buckets for the addition of alloying constituents, a crucible tilting mechanism, a utility rod for breaking any bridges of the metal which may form in the crucible, an immersion thermocouple and a viewing port or ports.

An example of a commercial vacuum melting furnace which can be adapted for either resistance or induction heating is the Vacuum Industrial Applications Ltd. model F2 (Fig. 14.11). The crucible (height: 6 in.; dia: 2 in.; capacity: 2 lb of copper) is supplied in graphite, alumina, zirconia or thoria. The horizontal cylindrical chamber (dia: 24 in.; depth: 18 in.) is evacuated to about 5×10^{-5} torr with a diffusion pump of speed 300 litre/sec at 10^{-4} to 10^{-3} torr. The self-supporting molybdenum element used for resistance heating (Fig. 14.3(*b*)) is surrounded by a number of coaxial molybdenum radiation shields, all enclosed within a water-cooled stainless steel mantle. Alternatively, an induction-heating coil is placed coaxially around a ceramic crucible. This coil is supplied with a.c. from a valve oscillator (Philips Electrical Ltd. high frequency induction heater) and is capable of melting 2 lb of copper in 60 sec. Bottom pouring with a liftable stopper rod is practised. A larger general purpose vacuum furnace is shown in Plate 12).

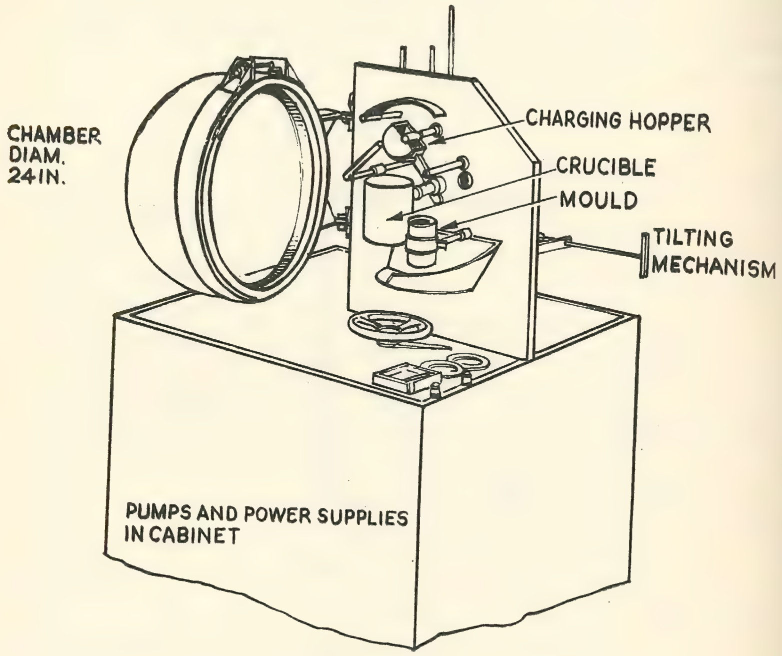

CHAMBER
DIAM.
24IN.
CHARGING HOPPER
CRUCIBLE
MOULD
TILTING
MECHANISM
PUMPS AND POWER SUPPLIES
IN CABINET

FIG. 14.11 A versatile vacuum melting furnace
(*Vacuum Industrial Applications Ltd.*)

Small vacuum induction furnaces for laboratory scale pilot plant studies have been described by Craw and Henry (CH1) and by Matthews (M23). The first (Fig. 14.12(*a*)) is a tilting vacuum furnace in which the crucible (capacity: 3 cm^3) is fixed in position in the vacuum chamber, which is rotated as a whole to pour the molten metal into the mould. The induction coil current is supplied by a 2 kW Lepel spark gap machine, small enough to be rotatable on the frame supporting the vacuum furnace and so enabling short coupling leads to be used. A flexible Tygon tube with an internal supporting coil of chromel wire is used to connect the furnace to the vacuum pumps, which are fixed in position.

The design due to Matthews (Fig. 14.12(*b*)) is for melts of up to 300 g; a hopper is included within the vacuum chamber to enable material (*e.g.* alloying constituents) to be added to the melt. A split copper mould is used. A typical straightforward arrangement is used for tilting the crucible by means of a mechanism connected through a Wilson seal in the wall of the vacuum chamber.

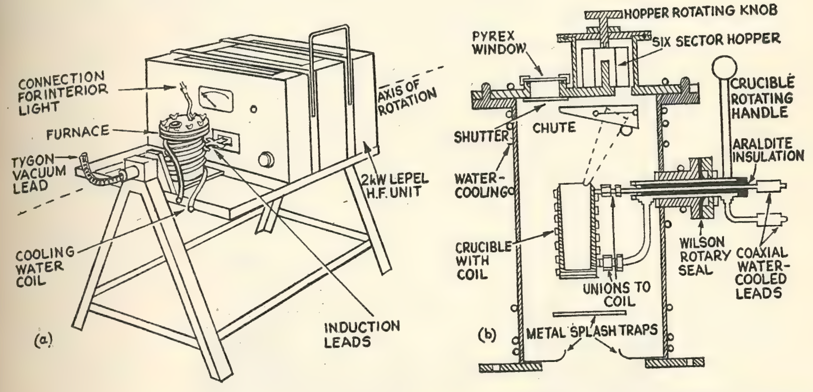

CONNECTION
FOR INTERIOR
LIGHT
FURNACE
TYGON
VACUUM
LEAD
COOLING
WATER
COIL
AXIS OF
ROTATION
2kW LEPEL
H.F. UNIT
INDUCTION
LEADS
(a)
HOPPER ROTATING KNOB
PYREX
WINDOW
SIX SECTOR HOPPER
CRUCIBLE
ROTATING
HANDLE
SHUTTER
CHUTE
ARALDITE
INSULATION
WATER-
COOLING
CRUCIBLE
WITH
COIL
UNIONS TO
COIL
WILSON
ROTARY
SEAL
COAXIAL
WATER-
COOLED
LEADS
(b)
METAL SPLASH TRAPS

FIG. 14.12 Laboratory-scale vacuum induction furnaces for melting metals

Several firms (*see* Appendix D) supply larger vacuum induction furnaces of the tilting crucible type for melting and casting metals. An outline description of the plant designed by Geraetebau-Anstalt Balzers (G.A.B.) for handling up to 25 kg (55 lb) of steel gives an idea of representative practice. The vacuum chamber is a double-walled vertical tank of inside diameter 32 in. with a double-walled lid; both the tank and lid are water-cooled (Fig. 14.13(*a*)). The vacuum seal between the spring counter-poised lid and the tank is a Neoprene O-ring. The water-cooled induction coil round the crucible is self-supporting (Fig. 14.13(*b*)) and is flanged on to the current lead so that it is vacuum-tight with fixture by two union nuts. It is supplied with a.c. at a frequency of 2 to 10 kc/sec and a power of 25 to 100 kW (melting times of about 30 min require about 2 kW of generator capacity per kg of steel, Malcolm, M22), from a motor generator, the maximum coil voltage being 250 V to avoid corona discharge. The supply current of up to 6000 amp is conveyed from the capacitor bank of the generator through a number of water-cooled cables; the lead-in serves also as the cooling-water feed to the induction coil, and is so fitted into the vacuum chamber wall that the coil with the crucible within it can be tilted. The arrangement of the mechanism for tilting the crucible is indicated by Fig. 14.13(*c*); it is similar to that of Fig. 14.12(*b*); indeed, Matthews based his small induction furnace on the Balzers plant.

The refractory crucible has a top ring and pouring lip (Fig. 14.13(*c*)), whilst for most types of charge the mould is of cast iron or steel. Observation ports provided in the chamber lid each have a screen to protect them from the deposition of metallic vapours; this screen is removed during observation by coupling to a lever (outside the vacuum chamber) which also connects to a wire brush (within the chamber) used to wipe off deposits on the glass window.

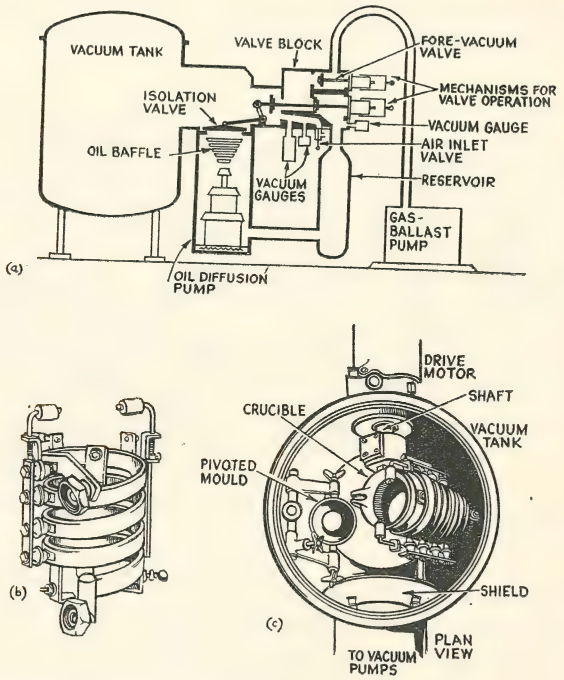


FIG. 14.13 A vacuum induction furnace capable of melting 55 lb of steel (*Geraetebau-Anstalt Balzers*)

(*a*) Arrangement of vacuum chamber and pumps
(*b*) The water-cooled induction coil
(*c*) View of crucible and mould within the vacuum chamber

The pumping is by a three-stage oil diffusion pump with a speed of 1000 litre/sec at 10^{-4} torr backed by a gas-ballast rotary pump. The high vacuum is monitored by a hot-cathode ionization gauge whilst a thermocouple gauge is used on the backing side.

The induction coil of this furnace can be replaced by a molybdenum heating element with radiation shields for radiation resistance heating; this arrangement permits vacuum sintering to be undertaken at temperatures up to 1600° C. With the induction coil, sintering temperatures up to 3000° C are possible.

The pouring of the molten metal into the mould in a vacuum furnace must be done slowly to enable gas evolved to be pumped away. For example, molten copper is poured at a rate of about 100 lb per min.

A means of adding material to the crucible charge during the melting operation is usually provided in a vacuum melting furnace. Two designs of charging bucket or hopper for this purpose are shown in Fig. 14.14. They are used to make additions when the required charge cannot be placed in the crucible when cold or for adding alloying constituents or, sometimes, deoxidizers. The type used in the G.A.B. vacuum furnace (Fig. 14.14(*a*)) consists of a cylindrical can divided into six sections and supported just under a port in the furnace main lid. This port has its own cover lid which is sealed by a Neoprene O-ring on closure. Material to be added to the crucible charge is placed in one or more of the six compartments, and an external handwheel enables any one of these compartments to be rotated into position over an aperture through which the contents can be dropped on to a scoop leading to the crucible. This scoop has an adjustment (operated from outside the furnace) to enable the rate of addition of the material to be controlled. A multiple charging bucket, operated manually via a vacuum seal or electrically by means of a solenoid, is shown in Fig. 14.14(*b*) (National Research Corporation).

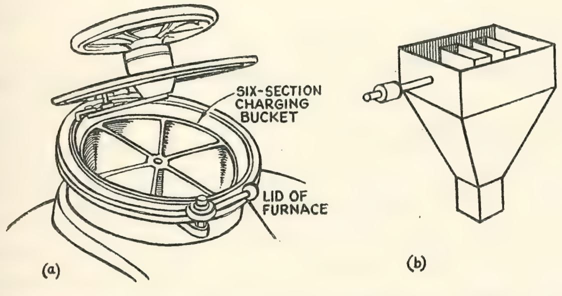


FIG. 14.14 Charging buckets for adding to a melted charge in a vacuum furnace

Barrett and Harper (BH2) have described in detail the 56 lb vacuum melting and casting furnace made by Edwards High Vacuum Ltd. In this plant, special insulation is used for the induction coil to enable voltages up to 400 V at 50 kW (frequency: 5 kc/s) to be used without danger of corona discharge. Also, a tubular ramrod assembly is arranged directly above the crucible, which is operated via a universal vacuum seal to break down bridges of metal which may form and also to admit gases such as hydrogen directly on to the surface of the melt. After the initial charge has been melted in the crucible, a bottom-opening bucket operated from a swinging arm may be set in position to add up to one-third of the total charge, whilst a small alloy charger permits alloying constituents to be added from any one of six cylindrical cans, also fitted with bottom shutters. Pumping is by a diffusion-ejector pump (unbaffled speed: 1300 litre/sec) able to handle large gas throughputs in the pressure range from 10^{-3} to 5×10^{-1} torr, with an air ultimate of 10^{-6} torr and able to work at a backing pressure as high as 3 torr so that a single-stage rotary backing pump may be used with full gas-ballast if required.

For pressure measurement three vacuum gauges are incorporated: an aneroid capsule manometer is used for the range 1 to 760 torr, a Pirani gauge for 5×10^{-3} to 10 torr and a Penning gauge for 10^{-5} torr to 5×10^{-3} torr. As the Pirani gauge filament is liable to become blackened during repeated furnace operations, it is deliberately blackened before use to prevent changes of the thermal emissivity upsetting the gauge calibration.

The temperature of the molten charge is measured by an immersion pyrometer based on a 5% Pt–Rh/20% Pt–Rh thermocouple. The pyrometer sheath is of metamic (Morgan Crucible Co., Ltd.) and is sealed to a stainless steel holder. The metamic sheath made from a molybdenum–alumina mixture is able to withstand 30 dips with immersion times of up to 2 min each. Two such pyrometers are provided; they are able to record temperatures up to 1800° C.

14.6. Vacuum Melting Furnaces for Large-scale Production; Semi-continuous Furnaces

Though a vacuum melting furnace with a crucible capacity of, say, 5 litre (corresponding to about 40 kg or 90 lb of steel) may be considered a unit of considerable size for the manufacture of special magnetic alloys or noble metals, it can hardly rank as of industrial magnitude in the production of high temperature alloys for aircraft jet engines or high strength steels for bearings or tools. As was pointed out by Darmara, Huntingdon and Machin (DHM1) the stress-rupture properties and the tensile strength of vacuum-melted high temperature alloys with a nickel base and appreciable quantities of aluminium and titanium as precipitation hardeners are so distinctly superior to those of the air-melted product that they are now demanded in quantity by the aircraft manufacturers.

To meet these demands, vacuum induction furnaces capable of processing several hundredweights or tons of metal have to be designed. It is only possible here to outline the present intensive activity in this field by quoting a few examples.

A desirable feature of production plant is semi-continuous operation so that the melting can be undertaken in a number of heats without opening the main furnace tank (melt chamber) to the atmosphere. Separate chambers which can be separated from the melt chamber by isolation valves or vacuum locks are used for the charging of raw materials (charging chamber) and the removal of the mould (mould chamber). As the main melt chamber does not have to be let down to atmospheric pressure as frequently as in batch operation, the advantages are (Moore, M21); (*i*) the system does not require repeated degassing; (*ii*) the crucible is kept hot so that power is conserved; (*iii*) the cooling times between heats required in batch operation are eliminated; (*iv*) the refractories used for the crucible lining and for electrical and heat insulation are not so frequently heated and cooled so that they are less liable to thermal damage.

A semi-continuous vacuum induction furnace for the melting and purifying of virgin raw materials and vacuum melted scrap at pressures of 10^{-3} to 10^{-1} torr is illustrated schematically by Fig. 14.15 (Moore, M21; Aksoy, A16). The induction-heated, tiltable crucible in the melt chamber is filled with the precharge from the charging chamber via a vacuum lock and chute. The preheated moulds on a flat trolley are introduced into the melt chamber via a vacuum lock and the crucible is then tilted for casting after the correct pouring temperature is attained. Two other small vacuum locks are included, one to enable a sample of the melt to be withdrawn for analysis before casting and the other for the insertion within the melt of an immersion thermocouple.

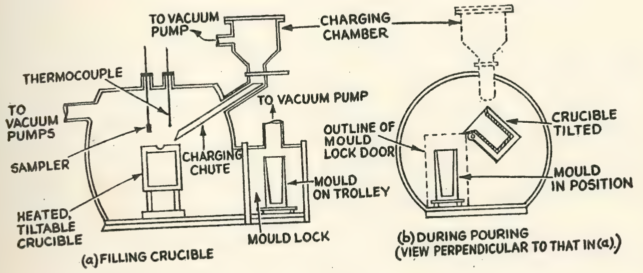


FIG. 14.15 Outline of semi-continuous vacuum induction furnace (pumping systems omitted)

Two examples of large commercial plants are the G.A.B. vacuum induction furnace with a crucible capacity of 30 litre with pumps capable of a speed of 8000 litre/sec (Plate 13) and the largest Heraeus furnace. The latter has a crucible volume of 75 litre surrounded by an induction coil of height 100 cm and diameter 52 cm able to handle 75 to 250 kW of power with a maximum current of 7500 amp. 230 litre/min of cooling water is demanded. The vacuum chamber is 170 cm high and 120 cm in diameter and is pumped by the following combination: a diffusion pump with a speed of 8000 litre/sec in the range 10^{-5} to 10^{-3} torr, two intermediate Roots pumps, the first of maximum speed 6000 m³/hour at 10^{-2} torr and the second with a speed approaching 1000 m³/hour in the range from 10^{-3} to 10 torr, the final backing pump being a two-stage gas-ballasted rotary with a displacement of 180 m³/hour.

Darmara, Huntingdon and Machin (DHM1) have described the 5000 lb vacuum melting furnace developed at the Utica Drop Forge and Tool Corporation. To provide the 1100 kW of power demanded for the induction coil, the coil voltage is designed to be 800 V to avoid an unwieldy conductor size. The induction coil is surrounded by vertical magnetic yokes which press radially on it to ensure rigid support, and also provide a magnetic flux path outside the crucible. Hence, magnetic material can be used close to the coil without danger of overheating and, moreover, the vacuum tank (12 ft in diameter) need not be non-magnetic and so can be made of mild steel. The inside diameter of the crucible is 25 in. for which size the optimum supply frequency for induction heating is 900 c/s. As this frequency does not, however, provide maximum stirring of the melt, the same induction coil is also fed with a second a.c. supply of 800 kVA at 30 c/s. A time of 60 sec is then sufficient to mix an addition of 3% aluminium and 3% titanium to a crucible charge of mass 2200 lb. The most satisfactory crucible lining material for adequate life was found to be 70% magnesia with 30% alumina.

This huge semi-continuous vacuum furnace has a separate mould chamber with its own vacuum system. Inside this mould chamber is a turntable 8 ft in diameter able to accommodate a variety of moulds. These moulds are either rotated into position under the crucible for casting or a movable tundish is used to direct the molten metal into successive stationary moulds. The mould chamber can be isolated by vacuum valves from the melt chamber so that the cast metal can be allowed to solidify slowly under vacuum and also new moulds can be installed whilst the melt chamber is recharged.

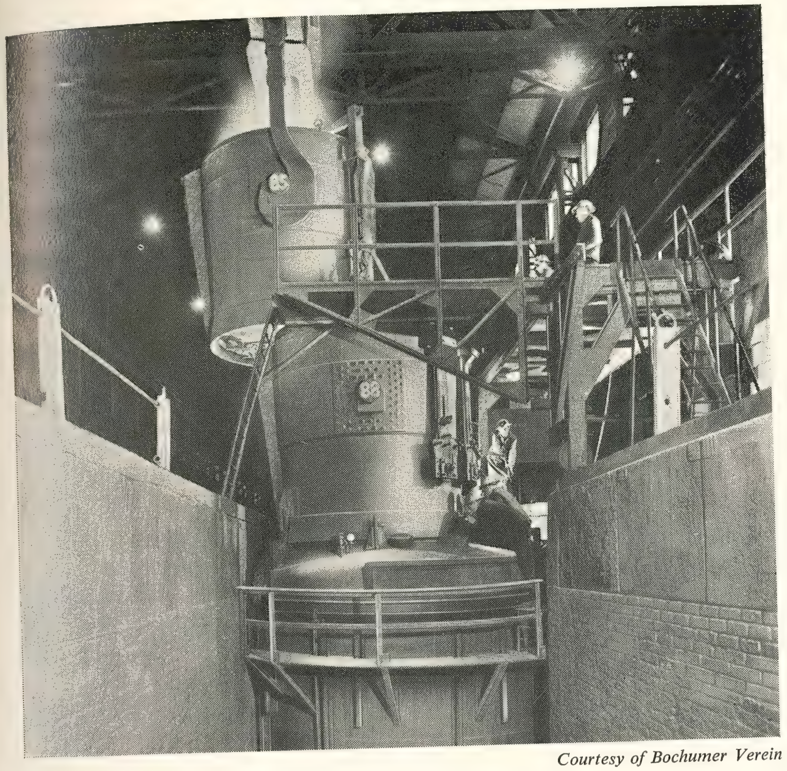
To enable material to be added to the melt, a vacuum-locked mechanism which can be loaded with 2400 lb of metal in 12 separate compartments is installed with the main vacuum tank. The contents of each of these compartments can be fed at a controlled rate into the main crucible by a screw feeder device. Provision is also made for samples to be withdrawn from the melt via vacuum locks so that they can be analysed spectrographically.

A manifold 4 ft in diameter connects the melt chamber to the pumping system. Twelve 16 in. port diameter diffusion pumps are used, two Roots pumps as intermediaries and two mechanical backing pumps. Before casting is begun, the pressure is reduced to below 10^{-3} torr; the chambers can be evacuated to 10^{-2} torr in 7 min, provided the pumps are hot.

14.7. Vacuum Arc Furnaces

A number of refractory metals with high melting points cannot be melted satisfactorily in vacuum induction furnaces because, in the molten state, they attack the ceramic (alumina, magnesia, zirconia, etc.) or graphite of which the crucible is made. Examples of such metals are columbium, molybdenum, tantalum, titanium, tungsten, vanadium and zirconium. The ideal practice would therefore be to melt these metals without their being in contact, when hot, with other materials. A valuable approach to this problem is to melt the metal in an arc operated either in an inert gas or in the residual gas and metal vapour in an evacuated chamber. In addition to avoiding many of the difficulties associated with ceramics, the vacuum arc furnace enables high temperatures to be attained (up to 3000° C or more), and the metal is very well dispersed in the arc stream. Disadvantages are that gases present are more soluble in the molten metal at the higher temperatures and that these gases are ionized in the arc and attracted electrically towards the melt.

An early use of the arc furnace was to produce ductile tantalum for incandescent lamp filaments (Bolton, B35; Siemens, S31; Pirani, P16). The apparatus used consists essentially of two water-cooled electrodes passing through rubber bungs in the top and bottom necks of a hard glass bulb (dia: 30 cm) which is evacuated by a two-stage mechanical rotary pump. These electrodes can be adjusted in position by hand from outside. One of them leads to an activated arc-stabilizing cathode which prevents the cathode spot from wandering when the pressure falls below about 10^{-2} torr and the other



Courtesy of Bochumer Verein

Plate 14

Plant for the vacuum stream degassing of molten steel (*see* p. 494) is an anode lead in the form of a nickel cylinder (Fig. 14.16). The pre-pressed tantalum powder cylindrical pellet is placed on a tantalum sheet of thickness about 2 mm. This sheet rests on a water-cooled nickel block mounted on the anode. The cathode consists of a tantalum pellet of irregular shape mixed with tantalum oxide; this is superficially fused by an arc in air at reduced pressure. Alternatively, rods of 5 to 7 mm dia made from a pressed and sintered mixture of tungsten powder and barium oxide may be used as arc stabilizing electrodes (Bauer and Schulz, BS4).

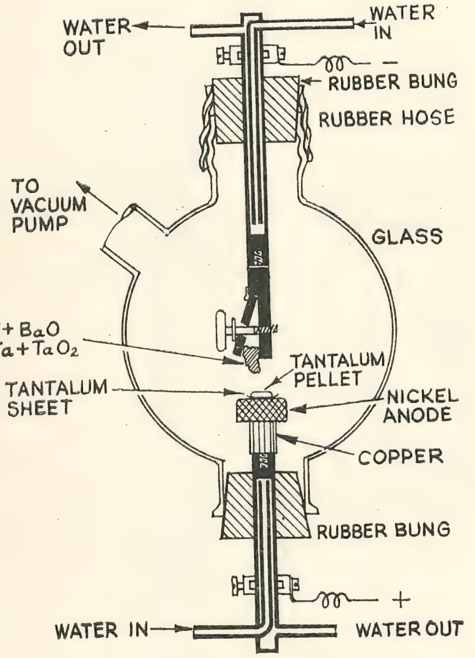


FIG. 14.16 An early design of vacuum arc furnace

The arc is made to strike by slight compression of the rubber bungs so that the cathode touches the tantalum sheet. It is then drawn on to the surface of the tantalum pellet and kept there until the pellet melts just slightly beyond half-way. This can be judged by slight vibrations of the surface. The cathode spot is then moved away from the pellet and the current switched off. After cooling, the half-fused pellet is withdrawn and arranged so that the fused face now touches the tantalum plate on the anode. The other half of the pellet is then melted by the arc.

For a pressed tantalum pellet of 80 to 100 gram in mass (*i.e.* about 8 cc) currents of the order of 50 to 300 amp were used with an arc voltage of 50 to 80 V for melting. During melting the pressure may rise from 5×10^{-3} to about 5×10^{-2} torr.

An alternative procedure is to degas the pressed tantalum powder piece in vacuum and then do the melting in an arc formed in admitted neon gas at a pressure of 1 to 3 torr.

In modern technology, two main methods have been used: (*i*) an arc is struck between the metal being melted and a tungsten-tipped water-cooled electrode; (*ii*) an electrode of the metal itself is actually consumed by the arc and the molten metal drops into a water-cooled crucible which forms the other electrode. Of this second type of vacuum arc furnace, two technical variations exist, (*a*) a consumable electrode (so-called consutrode) non-pouring furnace and (*b*) a consutrode pouring furnace. In current industrial melting of refractory metals, by far the majority of vacuum arc furnaces are of the non-pouring consutrode type and the water-cooled crucible is most frequently made of copper though aluminium and stainless steel have also been used.

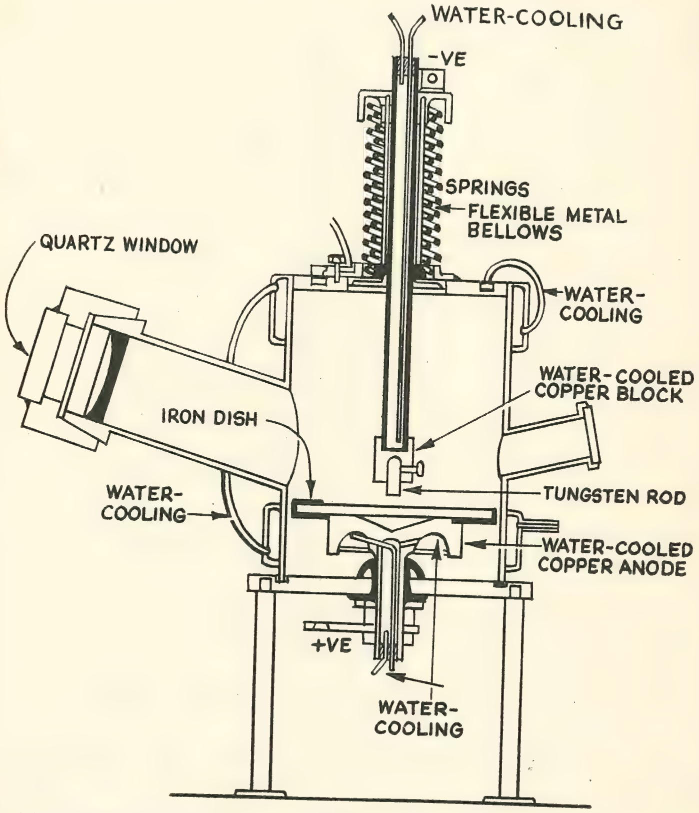


FIG. 14.17 Vacuum arc furnace with tungsten cathode and water-cooled copper anode (*after Kroll*)

A vacuum arc furnace with a permanent tungsten rod cathode designed by Kroll (K16) for the melting of titanium to make small 'buttons' of this metal is shown in Fig. 14.17. The cathode is a short rod of tungsten (preferably thoriated tungsten) which is clamped or preferably nickel-brazed to a copper block attached to the end of a water-cooled current lead. The cathode position can be adjusted as the vacuum seal around the current lead in the top of the stainless steel vacuum tank is in the form of a metal bellows with spring-loading. The anode in the base-plate of the tank is a water-cooled copper crucible. Two viewing ports are provided at the ends of side-tubes in the tank wall. The arc is struck in continuously admitted argon at a pressure of 50 torr, this pressure being necessary to ensure a stable arc. The total power consumption in this arc furnace is about 3·5 kW.

As the arc plays on the surface of the metal charge within the water-cooled anode crucible, melting takes place but with rapid subsequent solidification and where the bulk of the metal against the cooled walls of the crucible remains solid. In effect, fusion of the melt is therefore within a bath of the solid metal itself. Thus, although the metal to be melted may have a melting point as high as 3000° C, the cold walls of the crucible are not damaged and contamination of the melt by the copper of the crucible is negligible.

A disadvantage of this type of vacuum arc furnace is that small particles from the tungsten anode may be released in the arc and fall into the melt. Moreover, excessive gas evolution and splashing of the melted metal may occur so that alloying with the tungsten electrode takes place. The tungsten electrode has a limited life (often not more than a few minutes with the arc on); graphite has been used as an alternative but it is difficult to reduce carbon contamination of the melt. The consutrode technique is therefore preferred.

A typical small commercial vacuum arc furnace with a permanent cathode of thoriated tungsten is the Heraeus model L200d. Briefly, the specification is as follows: water-cooled crucible of diameter 11 cm and height 12 cm able to contain about 2 kg of metal; diameter of thoriated tungsten electrode, 10 or 15 mm; arc current, 100 to 1000 amp; ultimate vacuum, 5×10^{-3} torr (two stage mechanical rotary pump used); pumping speed at 10 torr, 200 litre/min. It can be used to make small ingots or 'buttons' of refractory metals, metal carbides and borides.

A **consumable electrode (consutrode) vacuum arc furnace** for the production of molybdenum rods about $5\frac{1}{2}$ in. long by $1\frac{3}{4}$ in. dia is shown in Fig. 14.18. (Hopkin, James, Moss and Pickman, HJMP1.) The steel vacuum tank *A* is connected to the pumping system by a manifold *G*. Into the top of this tank is fed the electrode *B* made from a very pure, pre-sintered molybdenum rod of about 6 ft in length and 1 cm dia. The driving mechanism *D* feeds this rod centrally down into a water-cooled copper mould *C* (*see also* Fig. 14.6). The vacuum seal necessary where this rod enters the top of the vacuum tank is a modification of the Wilson seal consisting of three dished Neoprene seals where the space between the second and third disc is $3\frac{1}{2}$ in. long and is evacuated by an auxiliary mechanical rotary pump.

A d.c. arc is struck between the molybdenum rod, which is the cathode, and a molybdenum disc inserted at the bottom of the water-cooled mould as anode. The arc is controlled in such a way that the molybdenum rod electrode is consumed at the rate of about 1 gram per sec. To arrange this, a current of 1200 to 1300 amp is necessary with a thyratron controlled arc of length $\frac{3}{4}$ in. and a p.d. across anode and cathode of about 35 V.

The ingot of molybdenum within the mould builds up gradually with only a small pool of liquid molybdenum in the centre of the mould at any time. The pumping system comprises a three-stage oil diffusion-ejector pump of speed 1000 litre/sec at 10^{-3} to 10^{-4} torr and a mechanical backing pump. Before the start of the melting operation the pressure is about 2×10^{-5} torr which rises to about 10^{-4} torr during the melting.

A critical feature of this and other vacuum arc furnaces and, indeed, of many types of vacuum casting plants, is the water-cooling of the mould. It is difficult to calculate from first principles the water flow rate required because a quasi-static water film forms on the inside wall of the jacket against the charge and the temperature gradient is extremely steep.

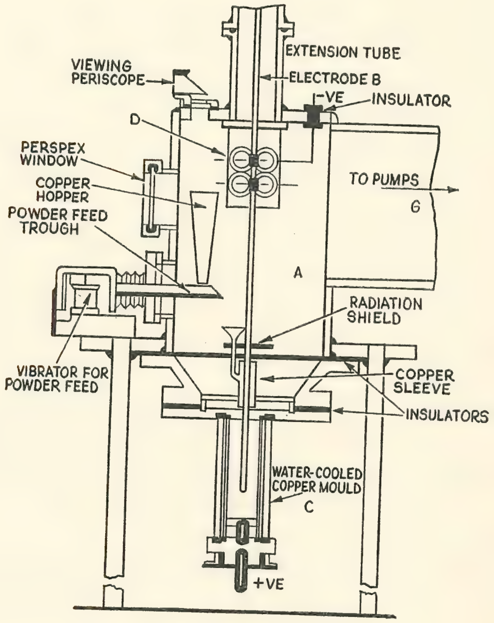


FIG. 14.18 Schematic diagram of vacuum arc furnace of the consutrode type for the casting of molybdenum rods

The essential part of the mould used by Hopkin *et al.* is a copper tube about 7 in. long with an inside diameter of $1\frac{3}{4}$ in. and a wall thickness of $\frac{5}{32}$ in. (Fig. 14.6). The parts of the mould are assembled and sealed by Neoprene O-rings, leaving an annular space $\frac{1}{4}$ in. wide for the water flow, which enters tangentially through an inlet of $1\frac{3}{16}$ in. internal diameter at the bottom of the mould and leaves at the top. For 40 kW of power in the arc, a water flow rate of 6 gall per min is needed.

In the consutrode vacuum furnace the arc is usually maintained within the metal vapour between the electrodes though an inert gas filling is also used in some cases. Without inert gas, the arc will only be maintained stably if sufficient metal vapour is available. This demands a large starting current and an adequate arc power depending on the vapour pressure of the metal at the temperature concerned (Fig. 14.21), the electron emission from the heated metal electrode, the dimensions of the electrodes and their geometry within the vacuum tank.

For the melting and refining of molybdenum and columbium by the vacuum arc cast process, Sayre and Stoph (SS4) recommend an arc current in excess of 2500 amp per sq in. of electrode area with a p.d. across the arc of 25 to 35 V. The p.d. across the arc plasma (the total p.d. is this plasma voltage drop plus those occurring at the anode and the cathode) is affected by the pressure of gas and the metal vapour in the arc; to ensure stable operation it is best, therefore, to have a total arc length not greater than 10 mm. An arc p.d. above 35 V gives rise to undesirable electrode burn off and the formation on the electrode of multiple tips.

The melt dropping from the cathode freezes too rapidly and so cannot be adequately purified and degassed if the arc current density is too low; on the other hand, too large a current density causes the metal to flow up the walls of the mould to leave a deep central cavity in the melt surface. The optimum range of current density values is decided by experimental trial. Within this range most of the metal reaches the mould in a highly super-heated liquid state, some of it is in the vapour state and a minute fraction is in the form of particles which fly off from the electrode. The molten pool of metal formed will extend to the walls of the ingot mould. This pool will be in a state of turbulence due to the force and rotational movement of the arc and thermal agitation. This 'stirring' is desirable to enhance purification and degassing of the melt. However, if the mould diameter exceeds $2\frac{1}{2}$ in. with an electrode surface of more than 1 sq in., it is best to place a coil carrying d.c. immediately around the ingot mould. The magnetic field produced helps to extend the molten pool of metal to the walls and promotes rotational stirring which assists uniformity of dispersion of alloy constituents. Furthermore, this field tends to constrict and hence stabilize the arc plasma.

For some 50 years, molybdenum, tungsten, tantalum and columbium were not melted but made available in the form of rods prepared by compression and sintering of the metal powder (Kieffer and Wirth, KW1). It is only with the advent of the vacuum arc furnace that these metals have been successfully melted and cast. Furthermore, for titanium and zirconium, sintering is not a particularly useful process so that their present availability in the pure state relies on vacuum arc furnacing. Molybdenum, tungsten, tantalum and columbium are available as a fine metal powder, whilst titanium and zirconium 'sponge' are produced by the Kroll process (§ 14.13). To fabricate a suitable electrode rod for a consutrode vacuum furnace the metal powder is subjected to extreme pressure and sintered; for large electrodes, smaller pieces of the metal are joined together by argon-arc welding.

Fig. 14.19(*a*) shows a consutrode vacuum arc furnace designed by Winkler (W12) in which the consumable electrode metal is loaded in powder form into a hopper in the upper part of the vacuum chamber; this powder is fed into a tube where it is sintered and degassed on heating it by the direct passage of a.c. so that a rod is formed which is pushed downwards into the arc where melting takes place, the final ingot being produced, as usual, in the water-cooled copper mould at the base of the vacuum chamber. Fig. 14.19(*b*) is a larger furnace (Stephens, Gilbert and Beall, SGB1; Miller, M24) for arc-melting Kroll zirconium sponge (*see* § 14.13). The crushed sponge is compacted in a steel die to form several small electrode bars. These rods are set up in an upper chamber to the furnace which is designed to enable a gloved operator to join the zirconium bars together by welding without the melting operation being interrupted. This furnace is operated in a mixture of 80% helium and 20% argon (because the use of rubber gloves forbids the use of vacuum) and is able to produce 200 lb ingots.

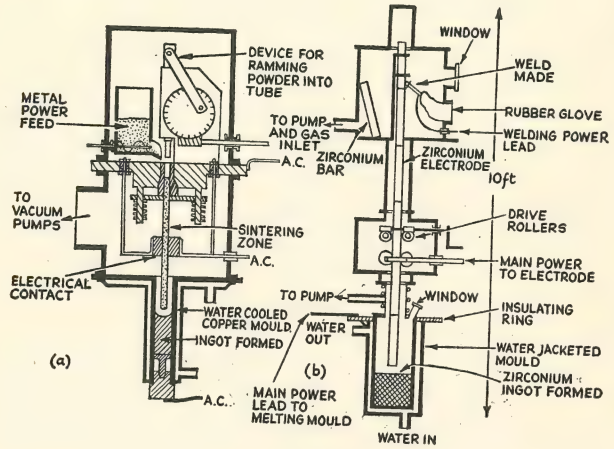

DEVICE FOR RAMMING POWDER INTO TUBE
METAL POWER FEED
TO PUMP AND GAS INLET
A.C.
TO VACUUM PUMPS
SINTERING ZONE
A.C.
ELECTRICAL CONTACT
WATER COOLED COPPER MOULD
INGOT FORMED
(a)
A.C.
WINDOW
WELD MADE
RUBBER GLOVE
WELDING POWER LEAD
ZIRCONIUM BAR
ZIRCONIUM ELECTRODE
10ft
DRIVE ROLLERS
MAIN POWER TO ELECTRODE
TO PUMP
WINDOW
INSULATING RING
WATER OUT
(b)
WATER JACKETED MOULD
ZIRCONIUM INGOT FORMED
MAIN POWER LEAD TO MELTING MOULD
WATER IN

FIG. 14.19

(*a*) Consutrode vacuum arc furnace (*after Winkler*)
(*b*) Consutrode furnace for the melting of zirconium (*after Miller*)

As an example of the many vacuum arc consutrode furnaces available commercially, a model made by Degussa Industrieofenbau is of interest. This versatile plant can be used with consumable electrodes or with auxiliary, water-cooled, permanent electrodes of tungsten or graphite. Ingot volumes of up to 5 litre can be cast. The p.d. across the arc is about 30 V under full load with a current of 1000 to 4000 amp depending on the diameter of the electrode and the metal concerned, if the consutrode method is used, and about 1500 amp with an auxiliary permanent electrode. The cooling water requirement is 10 gallons/min approx. Pumping is by an oil diffusion pump backed by a gas-ballast rotary pump with an intermediate Roots pump if large gas loads have to handled. Consutrode furnaces with arc currents as large as 25,000 amp have been planned.

Consutrode pouring vacuum furnaces of the so-called **skull melting type** are essentially similar to those previously described except that provision is made for pouring the crucible melt into a mould. The term 'skull' is used to describe the central cup-shaped depression in the surface of the solid metal within which the melt is formed from the consumable electrode. A copper crucible is used in place of the mould in the non-pouring furnace which, in one design, has an external water-cooling tube (Fig. 14.20(*a*)) so that, as heat is applied by the arc to the top of the central part of the melt, conduction through the sides and bottom of the crucible is at a sufficient rate to ensure that a frozen, solid layer of the metal covers the interior walls of the crucible. A depth to width ratio of 1 to 1·5 for the crucible gives optimum skull without unduly high arc currents. The molten pool of metal within this skull—only in contact with walls of the same metal so free from possible contamination by the copper—is poured to form a cast in a separate mould either by tilting the crucible or by bottom-pouring. Tilting (also known as 'lip-pouring') is preferred as bottom-pouring is reported to give inconsistent results (Beall, Wood, Borg and Gilbert, BWBG1). An outline diagram of a vacuum arc pouring furnace of the skull type based on a design described by Facaros, Carnahan and Bianchi (FCB1) is shown in Fig. 14.20(*b*).

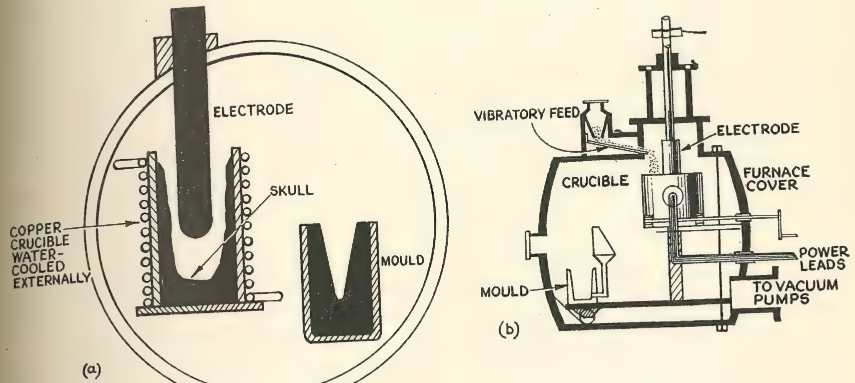

ELECTRODE
SKULL
COPPER CRUCIBLE WATER-COOLED EXTERNALLY
MOULD
(a)
VIBRATORY FEED
ELECTRODE
CRUCIBLE
FURNACE COVER
POWER LEADS
MOULD
TO VACUUM PUMPS
(b)

FIG. 14.20 Schematic diagrams of vacuum arc pouring furnaces of the skull type

Outline of Some Processes in Vacuum Metallurgy

The scope of vacuum metallurgy is so great and its study involves so many aspects of science and technology outside the scope of vacuum practice that it is only possible here to give brief details of some aspects of the processes undertaken and the results obtained.

14.8. Vacuum Heat Treatment

This term is used to denote the heating of a material without melting in a vacuum for the purposes of degassing, annealing, ageing or brazing. The degassing of metals in vacuum takes place at a rate decided by the temperature which can be attained, the diffusion of gases through the metal (which becomes a more significant limiting factor the thicker the metal), the removal of gases from the metal surface and the gas flow from the furnace to the pumps. The maximum temperature permissible is limited by phase changes which may occur in the metal and by the vapour pressure of the metal. In this latter connection, and in relation to other aspects of vacuum metallurgy, the curves of vapour pressure against temperature for a range of metals are given in Fig. 14.21. For most alloys, the vapour pressure is less than that of their most volatile constituent. To ensure rapid diffusion of gas through the metal it should be in the form of thin sheets. To provide a minimum impedance

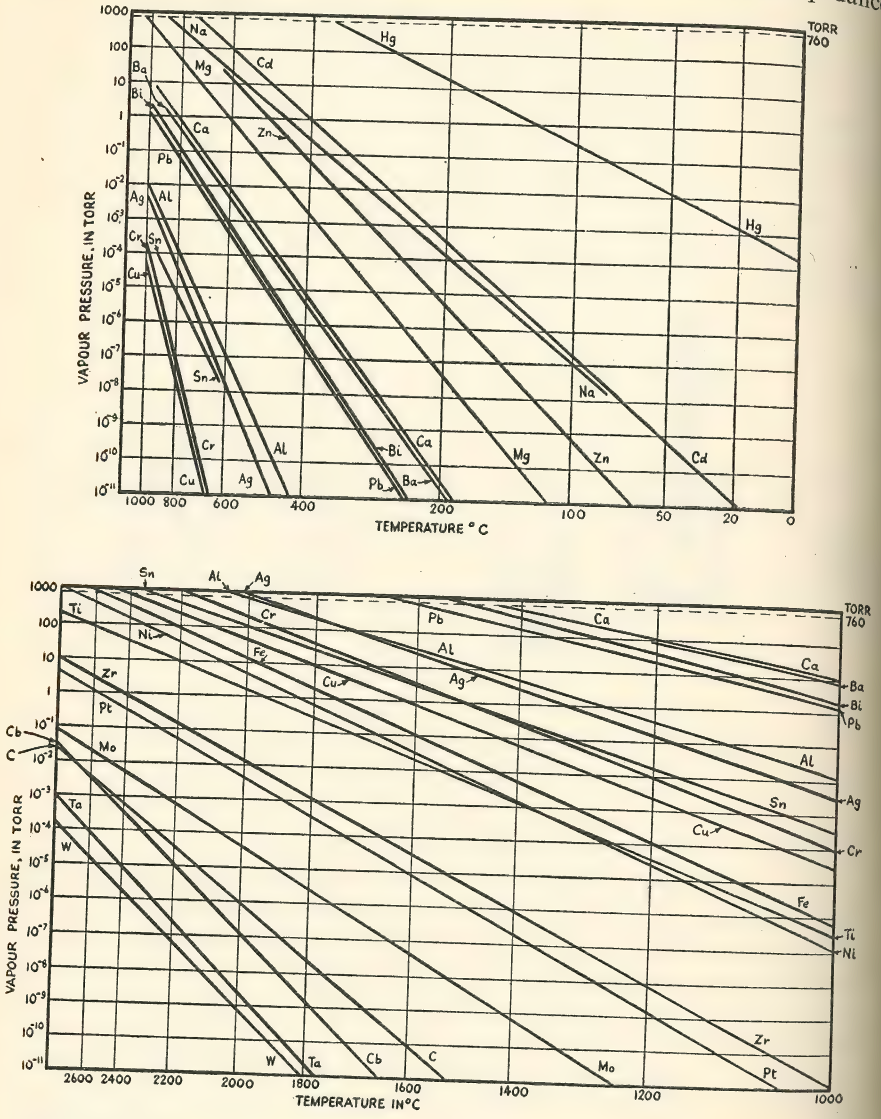


FIG. 14.21 Vapour pressures of various metals plotted against temperature

to gas flow from the heated metal to the pumps, as open as possible a path is necessary and, moreover, the metal sheets should be stacked parallel to one another with a separation between neighbours of at least $\frac{1}{16}$ in. and preferably $\frac{1}{8}$ in.

To convey an idea of the amounts of gas to be handled in large degassing plants the removal of hydrogen from titanium may be cited as an example. In several applications, the embrittlement of titanium due to its hydrogen content is inadmissible. Crites (C7) (*see also* Fazzalari, F13) reports that much of the hydrogen can be removed by heat treatment at 900° C at a pressure of 5×10^{-3} torr. He then considers the plant necessary to degas 500 lb of titanium parts per day, given that titanium contains initially 400 parts per million of hydrogen which is reduced to 100 parts per million by the degassing. 300 parts per million of hydrogen in 500 lb of titanium are readily calculated to occupy a volume of about 4×10^{6} cu ft at 5×10^{-3} torr. An oil ejector pump with an intake port diameter of 16 in. and a speed of 10^{4} cu ft/min at this pressure will remove this gas in about 10 hours, a time which will also allow for diffusion of gas through the metal. The mechanical backing pump required has a free air displacement of 250 cu ft/min. The titanium must be cooled to below 140° C before it is safe against action on exposure to the atmosphere. A two-zone vertical furnace is therefore used where the work in a suitable holder is hoisted from the hot zone into an upper water-jacketed cold zone. To heat the titanium in the hot zone, radiation heating elements with suitable radiation shields are used to provide a total of 60 kW of heat with the hot zone divided into three sections to ensure uniformity of temperature over the work. Reflective insulators are provided at both top and bottom of the work holder so that the hot and cold zones are separated irrespective of the position of this holder. With titanium parts of maximum dimensions 15 in. × 6 in. × 4 in., a vertical two-zone furnace tank 14 ft high by 4 ft in diameter is required.

A study of the free energy of dissociation of metal oxides (data is given by Giler, G19) shows that it is not usually possible to reduce oxides present in a metal by heating in vacuum. The admission of hydrogen at a pressure of about 1 torr is often beneficial here. For example, graphite is degassed at 1800° to 2200° C in a furnace with molybdenum or graphite radiation heating elements and shields. The admission of hydrogen assists the reduction of oxidized impurities which always exist in graphite.

Merrill (M25) reports that, whereas up till 1954 industrial plants for the removal of hydrogen from titanium were much used, titanium nowadays does not need such degassing except for special purposes because the manufacturers produce this metal with a lower hydrogen content than hitherto. Large plants for metal degassing have consequently been developed more for higher temperature degassing, annealing and brazing. Double-pumped furnaces (§ 14.3) have been designed with a $\frac{1}{4}$ in. thick inconel retort and Nichrome V heating elements in which temperatures of 1250° C can be maintained and which provide several thousand hours of service. Such furnaces are being used for the degassing and annealing in batches of up to one ton of zirconium and uranium alloys. To prevent surface contamination of the metal, the charge has to be thoroughly pre-cleaned and back-streaming oil from vapour pumps eliminated by the installation of cold-traps. Later developments include two-zone furnaces with internal heating within a cooled retort able to produce temperatures of 1700° or even 2200° C.

Attending the development of large degassing furnaces there has been great progress in plant for annealing and brazing metals in vacuum. Vacuum brazing (hydrogen at a pressure of 1 torr is often admitted to assist temperature uniformity, promote oxide reduction and inhibit metal evaporation) is now undertaken, for example, in the fabrication of large anode assemblies for power valves and the manufacture of intricate structures for aircraft, especially for jet engines. Useful data on brazing alloys for high temperature metals and superalloys is given by Huschke (H31), whilst design considerations are discussed by Gross (G24) (*see also* § 4.2).

An outstanding problem, or rather series of problems, remaining in vacuum heat treatment—as in other vacuum activities—is the design of plant for continuous operation involving vacuum locks for feeding in the material and removing it after treatment.

14.9. The Vacuum Treatment of Liquid Steel

Two main methods are currently used for degassing molten steel in large quantities, (*i*) vacuum stream degassing and (*ii*) ladle degassing.

In **vacuum stream degassing** the molten steel is released into the top of an evacuated chamber. As the stream falls into the vacuum it breaks up into drops because of the disruptive effect of the internal gas pressure so that the ready release of dissolved gas is favoured and a limited evaporation of volatile impurities occurs. In **ladle degassing** a ladle filled with the molten steel and slag cover is placed in a chamber which is evacuated as rapidly as possible to cause the release of dissolved gases from the melt.

Two procedures employed in vacuum stream degassing are illustrated in principle by Fig. 14.22(*a*) and (*b*). In (*a*) a tapping ladle (or an intermediate ladle fed from the tapping ladle or a number of such ladles) is erected above a vacuum tank which is pumped via the exhaust port shown. A casting ladle is placed within this vacuum tank. The outlet nozzle in the top ladle is closed by a stopper rod and also vacuum-sealed by a rupture disc, usually of aluminium. This ladle is filled with molten steel; on raising the stopper rod the rupture disc is melted by the steel which streams into the vacuum and finally into the casting ladle. The stream of steel breaks up into irregular drops; to assist the production of a narrow stream which does not splash the sides of the vacuum tank, a ceramic spray sleeve is often used. After the pouring is complete, air is admitted to the vacuum tank (inert gas is often admitted first to avoid the possibility of a dust explosion), the casting ladle filled with molten steel is removed and casting is then undertaken in air in the usual way. In case (*b*), known as **vacuum ingot casting**, the procedure is similar except that an ingot mould is placed in the vacuum tank, instead of the casting ladle, within which the melt solidifies after pouring.

Vacuum stream degassing is carried out in very large plants with melts of up to 150 or even 250 tons and pouring times as rapid as 10 tons per min (Plate 14). An outstanding advantage of the process is that the initial melt within the tapping or intermediate ladle is available as the produce of standard steel smelting furnaces such as the open-hearth furnace of the Siemens–Martin type, the Bessemer or the Thomas steel converter or an electric furnace. Marked gains from the point of view of economy result from the size of the plant. Taylor (T8) has given a comparison of the costs of various steel vacuum melting methods as follows: by vacuum induction furnace, 40 cents/lb; by vacuum arc consutrode furnace, 20 cents/lb; by stream degassing, 1 cent/lb.

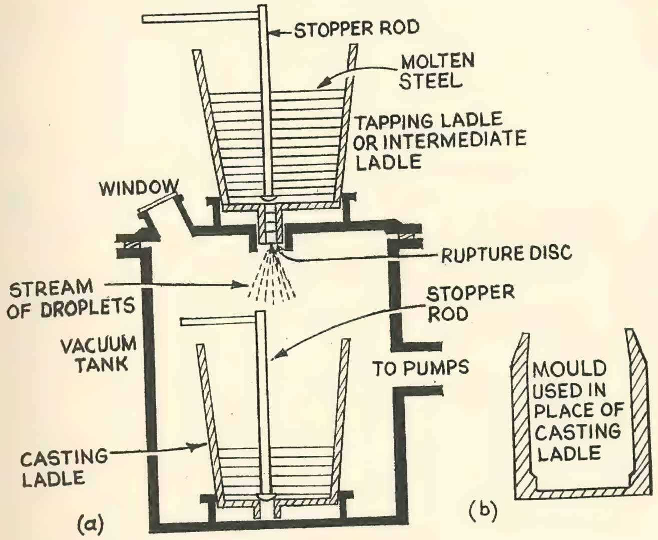


FIG. 14.22

(*a*) Vacuum stream degassing
(*b*) Vacuum ingot casting

The residual gas pressure produced within the tank before streaming is commenced is between 0·1 and 20 torr depending on the type of steel and the degree of degassing required. For the higher pressures, gas-ballast rotary pumps are usually employed. For example, the Bochumer Verein A.G. in Germany—pioneers in the vacuum stream-degassing of steel—use 10 Leybold gas-ballast pumps in parallel each with a free air displacement of 600 m^3/hour backed by a single gas-ballast pump of displacement 600 m^3/hour for a steam-degassing plant capable of handling melts of 40 to 100 tons, the vacuum tank being approx 7 m in height and 4·5 m in diameter (Fig. 14.23(*a*)). Cleaning devices and drying filters are inserted in the system to protect the pumps from dust. For lower pressures of 0·1 to 1·0 torr the practice is to use either Roots pumps backed by rotary pumps or steam-ejector pumps. According to Taylor (T9) a pumping capacity of 16,000 ft^3/min (27,000 m^3/hour) is required at 0·6 torr per ton of steel poured per minute. This gas throughput can be provided by multi-stage steam ejectors with suction port diameters ranging from 16 to 42 in. An American plant described by Taylor in which pumping is by four steam ejectors in series with appropriate inter-stage condensers is schematically illustrated by Fig. 14.23(*b*).

Stream degassing is now a prominent process for the production of steels where it is essential to avoid flaking, the possibility of micro-cracks and the formation of voids. Such steels are necessary in the construction, for example, of turbine rotors, jet engine parts and boiler plants. Flaking and micro-cracking are prevalent in certain steels in which hydrogen is present to the extent of more than 1·5 p.p.m. As steel produced by non-vacuum processes is cast in air, voids often form unless large casts are cooled extremely slowly over a period of weeks to allow gas to diffuse outwards from the interior. Vacuum stream degassing reduces this possibility to such an extent that much more rapid cooling is permissible.

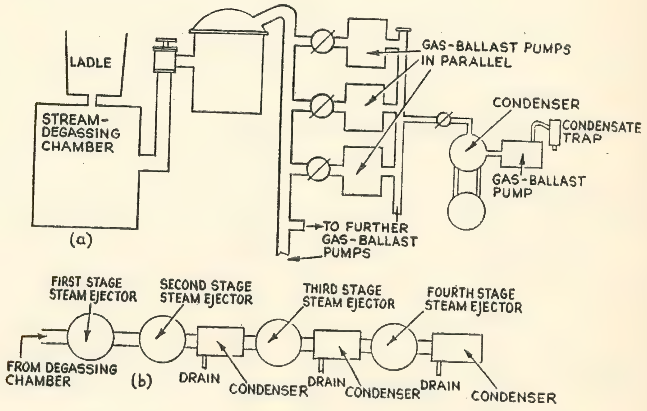

LADLE
STREAM-DEGASSING CHAMBER
(a)
GAS-BALLAST PUMPS IN PARALLEL
CONDENSER
CONDENSATE TRAP
GAS-BALLAST PUMP
TO FURTHER GAS-BALLAST PUMPS
FIRST STAGE STEAM EJECTOR
SECOND STAGE STEAM EJECTOR
THIRD STAGE STEAM EJECTOR
FOURTH STAGE STEAM EJECTOR
FROM DEGASSING CHAMBER
(b)
DRAIN
CONDENSER
DRAIN
CONDENSER
DRAIN
CONDENSER

FIG. 14.23 Pumping plants for stream degassing

The vacuum stream method and the degree of degassing obtained for various steels with corresponding improvements are considered in several papers of which recent ones may be mentioned by Tix (T10), Taylor (T8, T9), Tix, Bandel, Coupette and Sickbert (TBCS1) and Levaux and Nepper (LN1). Very briefly, the process prevents oxidation of the steel, enables carbon monoxide to escape readily and results in the removal of some 50 to 60% of the hydrogen content so that it is reduced to about 1 p.p.m., approximately 30% of the oxygen to leave between 10 and 60 p.p.m., whilst nitrogen is only slightly removed because stable nitrides tend to form in the steel. These reductions are not so great as in vacuum induction melting, but they are satisfactory for many purposes and it has not yet been possible to build an induction furnace able to handle melts of more than about 2 tons. The yield strength and the tensile strength of steels remain much the same on stream degassing, but the ductility is increased noticeably.

The process might well be applied in the future to the large scale degassing of other metals than steels.

As is pointed out by Winkler (W13) the vacuum stream degassing method is limited to the processing of melts with a comparatively high initial gas content because the release of considerable gas from the stream of metal is essential to ensure that disruption into droplets takes place. Moreover, the degree of degassing achievable is limited by the time of streaming.

In **ladle degassing** the ladle filled with the molten steel and slag is placed in

a vacuum chamber which is pumped as rapidly as possible for a considerable time (Fig. 14.24(*a*)). The melt boils violently and gas is released. On completion of degassing, air is admitted to the chamber and the steel cast in air. Samarin (S32) reports results achieved on ladle degassing a batch of 18 to 22 tons of liquid steel from a Bessemer converter at a pressure of 5 to 15 torr for 14 min. Before treatment deoxidation was carried out in the ladle with ferromanganese and ferrosilicon; after degassing, the more powerful deoxidizers aluminium or vanadium were introduced in the melt.

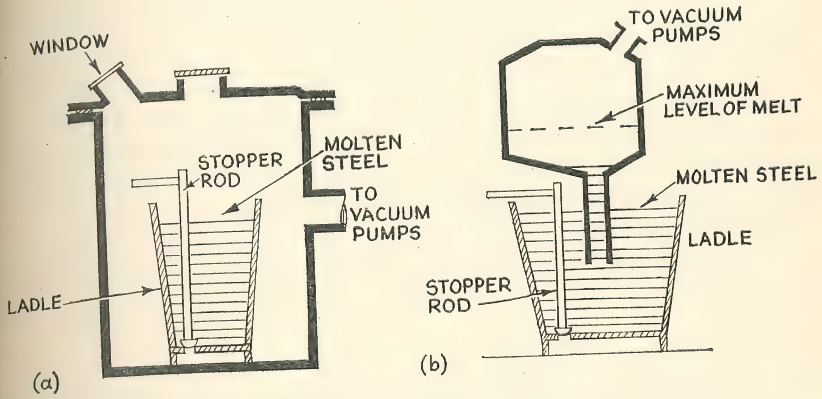


FIG. 14.24

(*a*) Ladle degassing
(*b*) Vacuum siphon degassing

A difficulty with ladle degassing is that the layers of the melt at the bottom of the ladle are not brought into contact with the vacuum to ensure effective degassing unless the melt is stirred. Perhaps the best way of arranging such 'stirring' of large masses of melt is to use the **vacuum siphon degassing** arrangement developed by Dortmunder–Hörder Hüttenunion (Harders, Knüppel and Brotzmann, HKB1) and also by Heraeus GmbH (Fig. 14.24(*b*)). In this installation, the melt (from a conventional steel melting furnace or of non-ferrous metal) in a ladle is connected by a tube to the pumped and heated degassing chamber above it. Part of the melt is introduced into this degassing chamber on raising the ladle and is made to flow back again on lowering this ladle. The degassing chamber is so shaped that the melt within it has a large surface area for a small depth of liquid. Raising and lowering of the melt into this degassing chamber a number of times ensures effective degassing of the whole of the melt because the large degassing melt surface is renewed repeatedly and because of turbulence in the melt during the flow in and out. The degassing chamber is exhausted by Roots pumps backed by gas-ballast rotary pumps. This method results in a greater degree of removal of hydrogen, oxygen and nitrogen than is possible with either the stream-degassing or the ladle-degassing methods.

Barret and Harper (BH2) allege that the stream-degassing method affords limited improvement in the treatment of special alloys (*e.g.* nickel chromium steels) because the hydrogen reduction is little better than 50% and, for melts of one ton or less, the temperature drop during the process demands either a high degree of superheat before treatment or reheating after treatment. Vacuum induction furnace heating is therefore favoured for the degassing of small tonnage melts of special alloys but, as the usual procedure is costly, Edwards High Vacuum Ltd. have developed an induction heated tilting vacuum furnace (crucible dia: 20 in.; height: 32 in., capacity 15 cwt of steel) which is charged with liquid steel alloy *melted in air* in the normal manner. This process has been termed **induction degassing**; it utilizes a h.f. induction coil fed with power from a motor generator set and arranged, by use of a change-over switch, to supply energy either to an air melting furnace or the vacuum furnace which are both installed as a duplex plant. As the total process time in the vacuum furnace is 15 min at a pressure of 0·6 torr (Roots pump backed by gas-ballast pump used) one degassing unit can be used to process the liquid charges obtainable from several air-melting furnaces.

For a 15 min induction degassing treatment of 15 cwt of steel alloy (Cr 18%; Ni 8%) the hydrogen content is reduced from 17 to 3 ml/100 g (*i.e.* by more than 80%), lead is removed completely, and carbon is reduced by as much as 50%.

14.10. The Melting of Metals in Vacuum Induction Furnaces; Addition of Alloying Constituents

Vacuum resistance furnaces were used before 1920 by Rohn (R22) to degas nickel–chromium alloys in melts of up to 650 lb. Subsequently, he used vacuum induction heating and, by 1939, was melting charges of 5 tons. In addition to its use in degassing melts, induction heating provides the most flexible means of preparing alloys in vacuum for the following reasons: ample time is available for degassing at superincumbent gas pressures of 10^{-4} to 10^{-1} torr; oxidation is prevented so that deoxidizing additions to the melt like silicon, manganese and aluminium used in air-melting are unnecessary; alloying additions can be made with complete dispersion in the melt, which is inductively stirred; very reactive alloying additions like titanium and aluminium can be made in much larger quantities than is possible in air-melting procedures.

Moore (M21) gives outline details of the process of preparing steel alloys by vacuum induction melting. As the initial steel charge is heated in the refractory crucible there occurs degassing, evaporation of volatile constituents (particularly lead, antimony, selenium and magnesium), reduction of oxides by carbon with the evolution of carbon monoxide and the reduction of the crucible lining by carbon and iron. The most important deoxidation reaction is the result of oxygen combining with carbon to form carbon monoxide. Theoretically, the equilibrium concentration of oxygen in 1% carbon steel at 1600° C is 0·005% at a superincumbent carbon monoxide pressure of 760 torr which is reduced to 6 × 10^{-8}% if this pressure is reduced to 10^{-2} torr, as is readily possible in a vacuum induction furnace. At the limit, the

minimum oxygen content is probably decided by oxidation at the crucible refractory. Using fused magnesium oxide crucibles it is possible to obtain iron with less than 20 p.p.m. each of carbon and oxygen.

The degassing and carbon deoxidation must be completed before alloying additions are made to the steel melt from charging buckets or hoppers. If the addition is a volatile metal it may be necessary to prevent losses due to evaporation by admitting inert gas to the furnace tank for a time during the process depending on the vapour pressure (Fig. 14.21) of the metallic addition concerned. The melt is then re-degassed subsequently. Admission of argon to give a tank pressure of about 30 torr is also often undertaken before casting a steel melt to avoid 'low pressure porosity' (which may express itself in bubbles having a diameter of a few millimetres filled with gas at a pressure of about 0·1 torr) and so obtain a denser ingot. Slow casting is recommended, *e.g.* about 1 min for a 50 lb charge, and should be along the wall of the mould rather than vertically to its bottom.

Reactive alloying elements which may be added to vacuum melts but which are inadmissible in quantity to air melted metal are aluminium, titanium (both of which are essential constituents of almost all nickel-base high temperature alloys), boron, cerium, columbium, tantalum, zirconium, molybdenum and tungsten.

Certain alloys containing readily oxidizable elements prepared by vacuum induction melting exhibit much greater strength at high temperature than air-melted products and also markedly superior workability, ductility, electrical and magnetic properties. Not only may reactive elements be added but it is easier to control precisely their amounts; for example, the addition of boron to steel results in much improved mechanical properties; any boron present in the melt is oxidized and pumped away before the correct amount of boron required is added, the control being such that 15 p.p.m. can be attained to an accuracy of 5 p.p.m. (Darmara, Huntingdon and Machin, DHM1).

A comparison between vacuum cast and commercial oxygen-free copper shows the benefits of vacuum induction melting and degassing of non-ferrous metals. Table 14.1 (Malcolm, M22) shows the effects of vacuum degassing and casting on the gas content and sulphur content of copper ingots. The small increases in density and electrical conductivity are noteworthy and also the improved ductility expressed as a percentage elongation under a given mechanical stress. The vacuum cast copper was deoxidized by the addition of carbon (resulting in carbon monoxide evolution) where the commercial copper was produced by standard metallurgical methods.

Table 14.2 shows the effect of varying the degassing time and the gas pressure during pouring on the oxygen and hydrogen content of vacuum cast copper.

In addition to the use of vacuum induction furnaces for the production of pure, low gas content metals like copper, iron and nickel and for the preparation of special high duty steel alloys and also magnetic alloys (Randall and Scholefield, RS2), other applications which may be mentioned are those especially important in the nuclear energy programme such as the manufacture of alloys of bismuth with uranium, zirconium and cerium for use in liquid metal-fuelled nuclear reactors (Turnbull, T2), the vacuum melting and casting of uranium (Stephenson, S33) and the preparation of aluminium–uranium alloys.

TABLE 14.1

	Commercial oxygen-free copper	Vacuum cast copper
Hydrogen	$1{\cdot}2 \times 10^{-4}\%$	$10^{-5}\%$
Oxygen	$4{\cdot}5 \times 10^{-4}\%$	$2 \times 10^{-5}\%$
Other gases	$4 \times 10^{-4}\%$	$2 \times 10^{-5}\%$
Sulphur	$2{\cdot}3 \times 10^{-3}\%$	$6 \times 10^{-5}\%$
Density	8·922 g/cm^3	8·93 g/cm^3
Electrical conductivity[1]	99·4	100·3
Elongation	17%	20%

[1] Expressed as a percentage of international annealed copper standard.

TABLE 14.2

Degassing time, hours	Pressure during pouring, in torr	Oxygen $\% \times 10^5$	Hydrogen, $\% \times 10^6$
1	0·038	8·8	9
1	0·6	15·5	10
3	0·024	8·1	5·2
3	0·08	13·0	13
5	0·014	4·6	5
5	0·1	8·5	10

14.11. Vacuum Sintering

Vacuum sintering is concerned with the fabrication in the form of a rod, sheet or wire of refractory metals like molybdenum, tantalum, columbium, rhenium, tungsten, thorium and also alloys and carbides of these metals. The metal in powder form is pressed into the required rod or sheet shape and then heated in vacuum to as high a temperature as possible, limited only by the melting point of the metal. The heating process is usually carried out in a steel water-cooled chamber evacuated initially to a pressure of 10^{-3} torr or less by a vapour/mechanical pump combination with the use of Roots pumps for large plants. Electrical resistance heating is generally used though induction heating is also employed, especially for small, symmetrical shapes and for temperatures above 1500° C. The resistance heating is either by direct passage of the electric current through the rod formed from the pressed powdered metal or by radiation from a surrounding heater element of molybdenum, tantalum, tungsten or graphite in the vacuum (§ 14.4). The latter method is usually preferred because direct passage of the current through the rod results in end losses and so imperfect sintering of the ends; for example, a tantalum bar 60 cm long and with a cross-section of 3 × 3 cm may be sintered in vacuum by the passage through it of a current of 6000 to 8000 amp, but the end losses amount to 8% of the total power dissipated in the metal. To convey the large currents demanded, water-cooled electrodes and leads are used and provision must be made by a suitable spring-loaded movable support to allow for shrinkage of the metal shape during sintering.

The advantages of sintering in vacuum are that atmospheric action is avoided, the metal is degassed and surface films of gas and other impurities at the boundaries between metal particles are removed; the fusion together of the particles is therefore more complete.

Adequate pumping capacity for a given mass of metal must be provided. In the sintering of tantalum powder at 2000° to 2500° C, for example, the gas evolution takes place in three stages (Miller, M26): at 450° to 500° C, hydrogen is evolved; at 1500° C, gas is released probably due to the reduction of some impurity oxide by carbon present in the tantalum; at 2000° to 2300° C, final gas evolution takes place due to a lower oxide of tantalum.

Turnbull (T2) has described a method for the production of a thorium bar by cold compacting and vacuum sintering. The powder is enclosed within a thin-walled rubber tube with rubber plugs at the ends and supported straight by a perforated thin-walled aluminium tube. This tube is placed within a steel pressure vessel containing water with a small amount of soluble oil. The insertion of a plunger into the water applies pressure to the powder for 10 sec. The removed compacted bar is placed on a thoria-covered molybdenum sheet and inserted in a Mullite tube which is then heated in a horizontal vacuum furnace to a final temperature of 1350° C over a period of 5 hours. The final temperature is then maintained for 2 hours. At temperatures up to 200° C, water vapour is evolved from the compact whilst between 350° and 1100° C, gas evolution is due to decomposition of thorium hydrides. The pressure rises from an initial 10^{-4} torr to 2 torr at 1350° C and finally drops to 2×10^{-2} torr.

14.12. The Purification and Separation of Metals by Distillation or Sublimation

In the processes concerned, the metal or a mixture of metals (*e.g.* an alloy) is heated in vacuum so that evaporation or sublimation takes place and the volatilized material is collected on a condenser. The object is either to remove non-metallic impurities from the metal or to achieve the separation of the components of a mixture of metals. In the first case, distillation is practised to remove, for example, gaseous impurities from the liquid alkali metals sodium, potassium and lithium. In the second case, the refined metal can be the condensed distillate, provided it evaporates more rapidly at the operating temperature than the other components or it may remain in the crucible if these unwanted components are evaporated preferentially.

In practice, to achieve a sufficient rate of volatilization the vapour pressure of the metal to be refined must be 1 to 2 torr at the operating temperature (*see* Fig. 14.21). Moreover, such pressures are required to ensure that the metal vapour pressure is significantly greater than the pressure due to gas released during the heating. At vapour pressures of 1 torr or more, molecular distillation conditions do not apply so that the concentration of the various components in the vapour at a given temperature is proportional to pM rather than $p\sqrt{M}$ where p is the vapour pressure and M is the molecular weight of the component (Winkler, W13).

To remove corrosive gaseous impurities (hydrogen, oxygen and nitrogen) from the alkali metals, distillation in vacuum is practised at temperatures given in Table 14.3 (Turnbull, T2).

TABLE 14.3

Metal	Boiling pt, °C	Distillation temperature, °C	Volatile impurities	Non-volatile impurities
Sodium	883	300–400	H_2	N_2O, alkali earths
Potassium	760	250–300	H_2	K_2O, alkali earths
Lithium	1336	500–600	H_2, N_2	Li_2O, alkali earths

Horsley (H32, *see also*, Turnbull, T2) has described a plant for the distillation of sodium in vacuum (Fig. 14.25). The sodium is first heated in the auxiliary stainless steel container *C* which is evacuated to a pressure of about 10^{-2} torr. The liquid sodium is then transferred through an iron wire-wool filter and a specially designed stainless steel valve to the still, which is evacuated to a pressure of 10^{-5} to 10^{-4} torr. In this still the sodium is heated to 300° to 400° C and the condensed vapour is collected on an oil-cooled surface at 100° C. The liquid condensate drips into a receiver beneath the condenser surface and when sufficient metal has collected it is transferred to an evacuated glass storage apparatus via the air-cooled outlet valve. Most of this plant is constructed of stainless steel and all surfaces which come into contact with the sodium are shot-blasted and electro-polished. The construction is sufficiently robust to withstand an explosion and is such that it can be safely cleaned.

In the separation of metals by vacuum distillation, the process is the more successful the greater the differences between the rates of evaporation of the constituents at a given temperature. As the vapour pressure against temperature curves for the various metals (Fig. 14.21) tend to converge at the higher temperatures, separation by distillation is best at as low a temperature as possible (Winkler, W13). However, the temperature must be sufficiently high for the evaporation rate to be great enough to ensure a satisfactory yield in a reasonable operating time. The surface of an evaporating liquid must be clean, freedom from foreign matter and oxide films being particularly essential as otherwise the evaporation rate may be seriously reduced. For a metal evaporating from the liquid state, efficient stirring is necessary to ensure continual renewal of the surface and to permit gas evolution from the whole bath of the liquid.

The design of the condenser surface and the cooling of the condenser must ensure removal of the condensation heat as the metal collects. If the condensed metal is in the solid state, growth of its layer thickness as distillation proceeds results in an increase of the temperature of the surface layers on the condenser relative to that of the cooling liquid. Too great an increase of this temperature due to inordinate thickening of the condensed metal layer will result in a coarse crystal structure of the deposited metal and eventually to re-evaporation of the metal from the condensate.

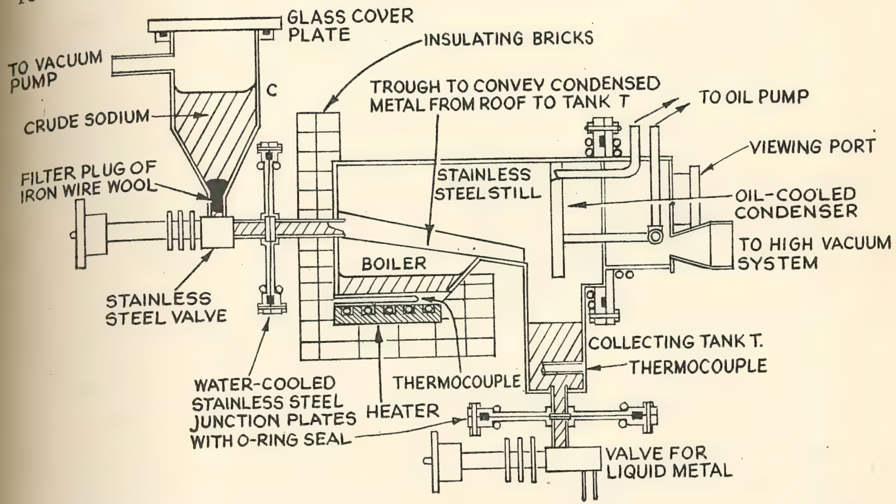


FIG. 14.25 Apparatus for the distillation of sodium in vacuum

Processes practised industrially for the separation and purification of metals include the reclamation of aluminium, magnesium and zinc from scrap, the separation of zinc from brass, and the purification of lead and of tin.

In a practical case of aluminium reclamation from scrap, the scrap contained 54% by weight aluminium with copper, zinc and silicon as major components and nickel, manganese, magnesium, lead, tin and titanium as minor impurities with less than 1% of each (Degussa Wolfgang Pamplet, 1953). The first step was to evaporate all the magnesium, the bulk of the zinc and lead and part of the manganese by heating the scrap in vacuum at 900° C. The intermediary residual product was then heated to 1100° C in vacuum in a second operation at which temperature the aluminium has a vapour pressure of 10^{-1} torr approx and distills off, leaving the other metals behind. In a third operation, the aluminium is melted in vacuum. Analysis of the product showed 99·81% aluminium, 0·1% tellurium, 0·08% silicon and traces of zinc and copper.

Figure 14.26(*a*) shows a vacuum resistance furnace with graphite rod heating elements designed by I.G. Farbenindustrie for carrying out the Beck process (Kroll, K16) for the vacuum distillation of magnesium out of aluminium–magnesium alloys. An alternative vacuum induction furnace for the same purpose designed by this firm is illustrated by Fig. 14.26(*b*).

According to Kroll (K16) the separation of zinc from brass has been attempted several times since 1914 but it seems that the process is best undertaken at atmospheric pressure as charging and tapping are facilitated. Spendlove and St. Claire (SS5) have described an induction furnace with condenser for the evaporation of zinc from aluminium–zinc alloys.

Lead can be effectively purified by vacuum distillation in that zinc can be effectively evaporated off whilst tin, silver, arsenic and copper are left in the residue; antimony and bismuth are not satisfactorily removed, however. The purification of tin results in the effective removal by evaporation of lead and arsenic, less satisfactory evaporation of antimony and silver, whilst iron and copper remain in the residue and their separation is incomplete.

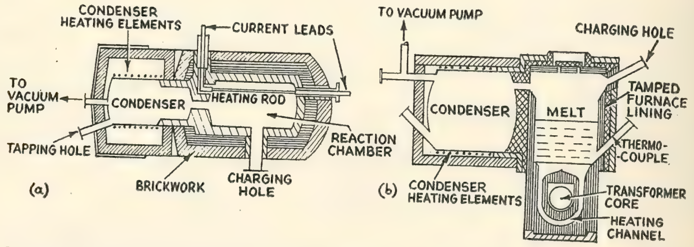


FIG. 14.26 Vacuum furnaces for the distillation of magnesium from aluminium–magnesium alloys (*a*) a resistance furnace; (*b*) an induction furnace

Kreusler and Pirani (KP1) evaporated nickel in vacuum from nickel–tungsten filaments containing 10% nickel. At temperatures from 1400° to 2000° C, pure tungsten was left.

The distillation of metals is also practised in vacuum thermal reduction processes in which the metal is extracted from an inorganic compound (*see* § 14.13).

14.13. Vacuum Thermal Reduction Processes for the Production of Metals

To obtain the metals barium, calcium, lithium, magnesium and strontium from an inorganic compound (*e.g.* an oxide or a suitable ore) processes have been developed in which the compound is heated with an added reducing agent in vacuum so that the metal required distils or sublimes off to a collecting condenser. Thermal reduction processes involving the use of vacuum but of a different kind are also used in the production of zirconium and titanium.

An early method by Guntz (G25) in 1906 involved the reduction of an oxide of a volatile metal in vacuum with a less volatile reducing agent so that the metal evaporated to a condenser. This process was applied to the production of barium and strontium by heating the oxide with aluminium in vacuum. For barium oxide the reaction is:

$$4BaO + 2Al \xrightarrow[0{\cdot}1 \text{ torr}]{1050^\circ \text{ to } 1200^\circ \text{ C}} 3Ba + BaO.Al_2O_3$$

where the temperature and pressure required are also given. Pellets made from powders of the oxide and the aluminium are heated in vacuum and the barium distils out of the mixture to be condensed on a water-cooled iron tube. The resulting material is granulated and pressed at 500° C in a protective atmosphere of argon and extruded into a copper tube which is hammered down cold to the required diameter.

In 1913 Matignon (M27) improved the process by using silicon in place of aluminium.

Like barium, calcium can be produced by the thermal reduction in vacuum of calcium oxide with aluminium, the reaction being:

$$6CaO + 2Al \xrightarrow[0.005 \text{ to } 0{\cdot}1 \text{ torr}]{1100^\circ \text{ to } 1175^\circ \text{ C}} 3Ca + (3CaO)Al_2O_3$$

High grade limestone is used which is calcined in a rotary kiln to produce calcium oxide which is melted to a fine powder (Kroll, K16). Fine powder aluminium is mixed with the calcium oxide and briquetted. The vacuum retorts are of chromium (28%) nickel (15%) steel alloy. These are placed horizontally in a gas-fired furnace so that their ends protrude by about 2 ft and are water-cooled to condense the calcium vapour.

A method which has been used extensively since 1938 for the production of magnesium is the Pidgeon process in which calcined dolomite is reduced thermally by ferro-silicon in vacuum. The reaction is represented by:

$$2(MgO.CaO) + \frac{1}{6}\,FeSi_6 \xrightarrow[0.005 \text{ to } 0{\cdot}5 \text{ torr}]{1100^\circ \text{ to } 1175^\circ \text{ C}} 2Mg + \frac{1}{6}\,Fe + (2CaO)SiO.$$

The production of magnesium by this method involves a sequence of operations of which only *one* is carried out in vacuum. The flow sheet for the process is (1) calcination of dolomite, (2) grinding of calcined ore and ferro-silicon, (3) mixing of calcined ore and ferro-silicon powders; (4) briquetting of the mixture, (5) *vacuum reduction and distillation*, (6) melting and casting (Miller, M26).

A steel retort used by Pidgeon and Alexander (PA2) was heated to a maximum temperature of 1175° C by gas or oil. Bagley (B36) has described a vacuum furnace for the Pidgeon process (Fig. 14.27) in which internal electrical resistance heating is used.

An alternative to the dolomite ferro-silicon process is that based on the reduction of calcined magnesite with calcium carbide. The plant used by Murex Ltd. for this method has been described by Miller (M26). The flow sheet is (1) calcination of magnesite, (2) grinding of calcined ore and calcium carbide, (3) mixing of calcined ore and calcium carbide powders, (4) briquetting of mixture, (5) *vacuum reduction and distillation*, (6) melting and casting. Only the fifth stage is undertaken in vacuum. The vacuum plant comprised 12 cylindrical retorts (length: 14½ ft; dia: 14 in.) within a gas-fired furnace (Fig. 14.28). The operating temperature was 1120° to 1140° C and the retorts were exhausted by mechanical rotary pumps, the permanent gas pressure being 0·5 to 1 torr after the large volumes of gas produced in the initial stages were pumped away.

The magnesium distilled to a split-tube steel condenser at the top of each retort which was air-cooled. After a heating cycle of 24 hours, the retorts were removed from the furnace and allowed to cool for 12 hours before removing the cover lids. Attached to the condensers were solid crusts of magnesium; these were removed and melted in air in steel crucibles with a flux consisting of a 50/50 mixture of magnesium chloride and fluoride. By agitation, a bath of clean metal was produced and cast continuously into slabs. During pouring in air, sulphur was dusted over the metal surface to provide a protective atmosphere of sulphur dioxide. 70 to 80 lb of magnesium of 99·9% purity were obtained from a retort charge of about 5 cwt of the mixture.

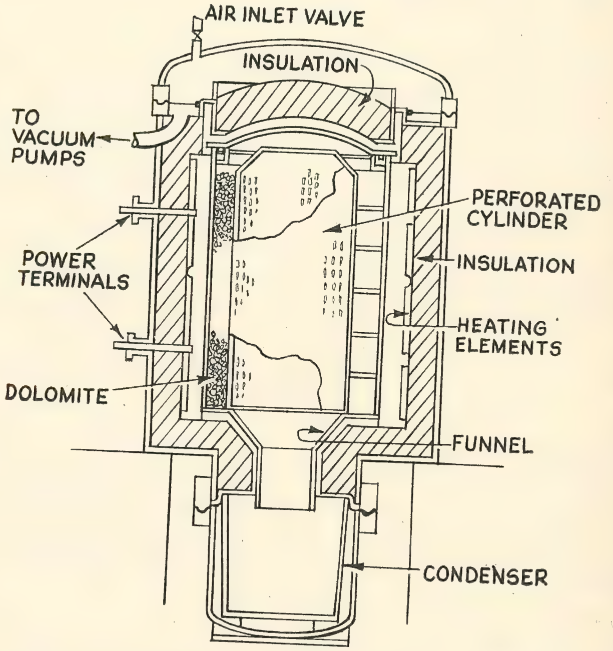


FIG. 14.27 Vacuum furnace for the production of magnesium by the Pidgeon process

Lithium is obtained by thermal reduction with aluminium of lithium hydroxide plus burned lime according to the reaction:

$$6LiOH + 4Al + 6CaO \xrightarrow[0\cdot005\text{ to }0\cdot1\text{ torr}]{1100^\circ\text{ to }1175^\circ\text{ C}} 6Li + 2[(3CaO)Al_2O_3] + 3H_2.$$

Alternatively, spodumene ($LiAl(SiO_3)_2$) is used in place of the hydroxide and lime when the reaction is:

$$LiAl(SiO_3)_2 + Al \xrightarrow[0\cdot005\text{ to }0\cdot1\text{ torr}]{1050^\circ\text{ to }1150^\circ\text{ C}} Li + \text{complex silicate.}$$

The chlorides or bromides of caesium and rubidium can be reduced to the respective metals by heating in vacuum with calcium in an evacuated chamber of heat-resisting glass. This process has been used for small quantities of these metals (Kroll, K16) and is the same as that often used to produce caesium in the manufacture of vacuum photoelectric cells (Yarwood, Y1).

Two processes are used for the commercial production of zirconium:

(1) Crude zirconium is heated in vacuum in the presence of iodine vapour. Zirconium tetraiodide vapour is formed which decomposes as it contacts a heated filament inserted in another part of the vacuum chamber to build up on this filament a rod of the metal of about ½ in. in diameter.

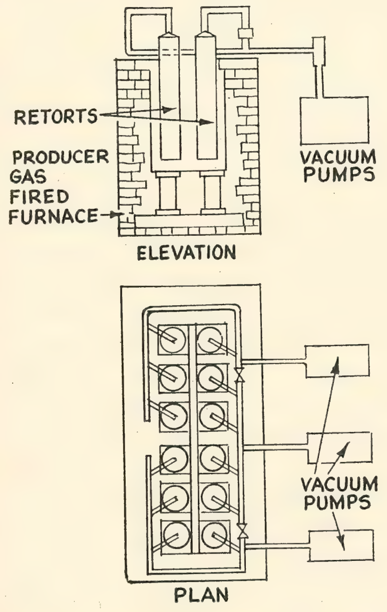


FIG. 14.28 Arrangement of vacuum furnace in the production of magnesium by the calcium carbide process (*after Miller*)

(2) The Kroll process (Kroll, Schlechten and Yerkes, KSY1; Kroll, Anderson, Holmes, Yerkes and Gilbert, KAHYG1). The zirconium ores are zircon sand ($ZrSiO_4$) and baddeleyite (ZrO_2). Carbon is added to the ore which is then smelted in an arc furnace to produce an impure carbide containing about 80% zirconium (Kroll and Stephens, KS3). The carbide is then chlorinated to produce raw zirconium tetrachloride. (This contains 2% hafnium; if, therefore, the zirconium is to be used in a nuclear reactor, *e.g.* for canning uranium fuel rods, its neutron capture cross-section must be kept low so the neutron absorbing hafnium must be removed by ion exchange or solvent extraction.) The zirconium chloride may then be purified and densified in a hydrogen atmosphere. The pure chloride is then reduced by fusing with magnesium in an atmosphere of argon or helium to produce zirconium sponge containing residues of magnesium chloride and magnesium. The magnesium and magnesium chloride can be separated out by vacuum distillation at 950° C. However, to remove traces of the magnesium chloride remaining (which render the zirconium useless for practical purposes) and

also hydrogen, the zirconium sponge is finally either melted in a split tube graphite resistor furnace or it is melted (and alloying additions made, if required) in a vacuum arc furnace.

Zirconium reacts with the usual refractory crucible materials, but graphite can be used with very little contamination. Miller (M26) stresses, however, that this contamination is sufficient to reduce the resistance of the metal to corrosion by certain chemicals, notably hydrochloric acid. For this reason, vacuum arc melting is preferred to the use of a graphite furnace. The type of furnace used is shown in Fig. 14.19(*b*).

To incorporate alloy additions, *e.g.* tin, within the zirconium, small tablets containing the alloying ingredients are fed individually from a circular vibratory feeder into the molten zirconium within the water-cooled mould of the vacuum arc furnace (Miller, M26). The homogeneity of the alloy is greatly improved if a magnetic field is set up in the molten metal by passing d.c. through a copper coil wound round the entire water jacket. The magnetic field causes the melt to rotate and promote mixing. A final stage to ensure consistently homogeneous ingots is to use ingots produced by the first arc melt (which is in a helium–argon filling as the use of rubber gloves, Fig. 14.19(*b*), prohibits the maintenance of a good vacuum) to make the consumable electrode for a second arc melt which is undertaken in vacuum. In an example given by Miller, a consutrode formed by joining together several 6 in. dia ingots is vacuum arc melted to form an ingot of 8 in. dia in a water-cooled mould.

The zirconium alloy, 'Zircaloy-2', is now preferred in nuclear reactor construction as it has better high-temperature properties than zirconium. It is prepared by adding the alloying ingredients to the vacuum arc melted zirconium. The percentages by weight of these additions are Sn, 1·45; Fe, 0·125; Cr, 0·10; Ni, 0·05. The vacuum arc skull furnace (§ 14.7) is also used for the production of casts of zirconium and its alloys (Facaros, Carnahan and Bianchi, FCB1). Titanium sponge is also produced by a similar Kroll process and may be similarly vacuum arc melted. Titanium sponge produced on the reduction of titanium tetrachloride by magnesium in the Kroll process contains about 15% magnesium chloride. A vacuum distillation process for removing this chloride is described in detail in the journal *Light Metals* (Anon, A17).

Appendices A, B, C, D

APPENDIX A

GASES AND VAPOURS

Ideal gas. An ideal or perfect gas is a theoretical concept for which the following assumptions are made:

(*i*) The molecules are minute hard spheres.

(*ii*) The volume occupied by the molecules is negligible compared with the actual volume occupied by the gas.

(*iii*) The molecules do not exert forces upon one another.

(*iv*) The molecules travel along rectilinear paths in a perfectly random fashion, *i.e.* all directions of motion are equally likely.

(*v*) On impinging upon the walls of the containing vessel, the molecules make perfectly elastic collisions.

For a gas, a change of direction of motion of a particular molecule only takes place when it collides with another molecule or with the walls of the containing vessel.

Those gases commonly encountered which approximate closely to ideal gases in their behaviour at normal pressures are hydrogen, nitrogen, oxygen, and the rare inert gases: argon, helium, neon, krypton and xenon. As the gas pressure is reduced and so the average distance between molecules is increased, ideal gas behaviour is more nearly approached.

A vapour is a gas at a temperature below its critical temperature. It can be condensed to the liquid or solid state by increase of pressure alone.

Critical temperatures and critical pressures (*i.e.* the highest pressure at which a vapour can exist in equilibrium with its liquid) for several gases are given in Table A1.

For an ideal gas it is readily proved that

$$p = \tfrac{1}{3}\, mnC^2 = \tfrac{1}{3}\rho C^2 \tag{A1}$$

where p is the pressure exerted by the gas, m is the mass of a molecule of the gas, there are n molecules of the gas per unit volume, ρ is the density of the gas, and C is the root mean square velocity of these molecules.

As the total kinetic energy, E, of the molecules in unit volume is $\tfrac{1}{2}\, mnC^2$, equation (A1) can also be written:

$$p = \tfrac{2}{3}\, E \tag{A2}$$

One mole (*i.e.* one gram-molecule) of a gas contains N molecules where N is Avogadro's number.

$$\mathrm{N} = 6{\cdot}023 \times 10^{23} \text{ atoms/mole.*}$$

This number N is the same for all substances.

Number of molecules per litre. One mole of an ideal gas at N.T.P. (0° C and 760 torr) occupies a volume of 22·415 litre. Hence the number of molecules per litre at N.T.P. is $6{\cdot}023 \times 10^{23}/22{\cdot}415 = 2{\cdot}687 \times 10^{22}$.

The number of molecules per litre at a pressure of 1 torr and temperature 0° C is therefore equal to $3{\cdot}54 \times 10^{19}$.

The number of molecules per litre at a pressure of 10^{-n} torr is $3{\cdot}54 \times 10^{19} \times 10^{-n} = 3{\cdot}54 \times 10^{19-n}$.

The gas constant R. If V is the volume occupied by a mole of gas, equation (A2) can be written:

$$pV = \tfrac{2}{3}\,\mathrm{N}E \tag{A3}$$

It can be shown empirically that

$$pV = \mathbf{R}T \tag{A4}$$

where T is the absolute temperature and **R** is the gas constant, which has the same value for all gases.

The gas constant R can therefore be defined as equal to two-thirds of the total translational energy of the molecules in one mole of gas at a temperature T equal to 1° abs.

$$\mathbf{R} = 8{\cdot}314 \times 10^{7} \text{ erg deg}^{-1} \text{ C mole}^{-1}.$$

Boltzmann's constant k is **R**/N. Hence $3\mathbf{k}T/2$ is the translational kinetic energy of a single gas molecule at T° abs.

$$\mathbf{k} = \mathbf{R}/\mathrm{N} = 1{\cdot}3804 \times 10^{16} \text{ erg deg}^{-1}$$

As

$$\tfrac{1}{2}\,mC^2 = \tfrac{3}{2}\,\mathbf{k}T$$

substitution in equation (A1) gives

$$p = n\mathbf{k}T \tag{A5}$$

The Maxwellian distribution of velocities. For a gas in a steady state in which there are n molecules per unit volume, the number of molecules whose resultant velocities lie between v and $(v + dv)$ is n_v, given by:

$$n_v = 4\pi n A e^{-hmv^2} \,.\, v^2 dv \tag{A6}$$

where,

$$A = \left(\frac{hm}{\pi}\right)^{\frac{3}{2}} = \left(\frac{m}{2\pi\mathbf{k}T}\right)^{\frac{3}{2}} \tag{A7}$$

and

$$h = \frac{1}{2\mathbf{k}T} \tag{A8}$$

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* Values of constants are given on the chemical scale on which the atomic weight of natural oxygen is taken to be 16·0000 exactly. On the physical scale, the mass of the nuclide, ${}^{16}_{8}\mathrm{O}$, is taken to be 16·0000 atomic mass units exactly. Atomic weights on the physical scale are about 0·03% less than on the chemical scale.

The average velocity of all the molecules, $\bar{v}$, is given by multiplying equation (A6) by v, integrating over the range from $v = 0$ to $v = \infty$ and dividing by n. Therefore,

$$\bar{v} = 4\pi\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \int_0^\infty e^{-hmv^2} \,.\, v^3 dv$$

$$= 2/\sqrt{\pi hm}$$

Substituting for h from equation (A8),

$$\bar{v} = \sqrt{\frac{8\mathbf{k}T}{\pi m}} \tag{A9}$$

From equations (A1) and (A5)

$$C^2 = \frac{3p}{mn} = \frac{3\mathbf{k}T}{m} \tag{A10}$$

Comparison of equations (A9) and (A10) gives:

$$\frac{\bar{v}}{C} = \sqrt{\frac{8}{3\pi}} = 0{\cdot}921 \tag{A11}$$

The Maxwellian distribution of velocities may be represented graphically by plotting $4\pi nAe^{-hmv^2} \,.\, v^2$ from equation (A6) against v. A family of curves is obtained with the temperature as parameter. On one of these curves, the number of molecules having velocities between v and $(v + dv)$ is obtained from the area under the curve enclosed between vertical ordinates drawn through v and $(v + dv)$, where the velocity axis is horizontal.

At any given temperature, the curve has a maximum value corresponding to the **most probable velocity** of the molecules. This most probable velocity, α, is given by differentiating n_v with respect to v and equating to zero.

$$\therefore \quad \frac{dn_v}{dv} = \frac{d}{dv}\left(4\pi nAe^{-hmv^2} \,.\, v^2\right) = 0$$

$$\therefore \quad \alpha e^{-hm\alpha^2}\left(1 - hm\alpha^2\right) = 0$$

$$\therefore \quad \alpha = \sqrt{\frac{1}{hm}} = \sqrt{\frac{2\mathbf{k}T}{m}} \tag{A12}$$

on substituting for h from equation (A8).

The mean free path is the average distance that a molecule travels in a gas between collisions. It can be shown that this mean free path, λ, is given by:

$$\lambda = \frac{1}{\sqrt{2}\pi n\sigma^2}$$

where σ is the diameter of a molecule (*see* Table A1).

From equation (A5) it is seen that the number of molecules per unit volume, n, is inversely proportional to the pressure p at a given temperature. For a given gas at a given temperature, therefore,

$$\lambda = k/p \tag{A13}$$

where k is a constant.

For air at 20° C, the equation can be written in the convenient form:

$$\lambda = \frac{5 \times 10^{-3}}{p} \text{ cm}$$

where p is the gas pressure in torr.

In the case of electrons in a gas, of negligible size compared with the gas molecules, and hence considered as points in the gas, the expression for the mean free path becomes:

$$\lambda_e = \frac{4\sqrt{2}}{\pi n \sigma^2} = 4\sqrt{2}\lambda = 5{\cdot}6\lambda \tag{A14}$$

The number of molecules per unit volume which describe a path longer than a given distance L in the gas, where the mean free path is λ, is n_L given by

$$\frac{n_L}{n} = e^{-L/\lambda} \tag{A15}$$

The number of molecules striking unit area of a boundary in the gas per second.

Let there be n molecules per unit volume with an average velocity $\bar{v}$ where the mean free path is λ. The total distance traversed by these molecules in unit time is $n\bar{v}$. Let ν be the number of collisions occurring between molecules in unit volume per unit time. Each collision terminates two free paths. Hence the total distance traversed by the molecules in unit time is also given by $2\nu\lambda$. Therefore,

$$2\nu\lambda = n\bar{v}$$

and

$$\nu = n\bar{v}/2\lambda.$$

As two molecules are necessarily involved in a collision, the number of molecules per second coming straight from a collision in unit volume is 2ν or $n\bar{v}/\lambda$.

Consider the molecules which strike an element of area dA of a boundary surface in the gas. Those which are incident at an angle θ with the normal and are contained within the solid angle $d\omega$ and which, furthermore, come from a distance between l and $l + dl$ were contained in a volume element of $l^2\, d\omega\, dl$. The number of the molecules in this volume element which come straight from making an intermolecular collision is $\frac{n\bar{v}}{\lambda} l^2\, d\omega\, dl$. Of these, a fraction $\frac{dA \cos\theta}{4\pi l^2}$ travel in the direction towards dA, *i.e.* a number $\frac{n\bar{v}\, d\omega\, dl\, dA \cos\theta}{4\pi\lambda}$. Equation (A15) shows that a fraction $e^{-l/\lambda}$ travel the distance l without making a further intermolecular collision. The number which arrive at dA per second is therefore given by

$$\frac{n\bar{v}\, d\omega\, dl\, dA \cos\theta . e^{-l/\lambda}}{4\pi\lambda}.$$

For a given solid angle $d\omega$, l may have values from 0 to ∞, hence the number of molecules impinging on dA per second which come along the direction θ from within the solid angle $d\omega$ is

$$\frac{n\bar{v}\, d\omega\, dA \cos\theta}{4\pi\lambda} \int_{l=0}^{l=\infty} e^{-l/\lambda}\, dl = \frac{n\bar{v}\, d\omega\, dA \cos\theta}{4\pi}$$

To take into account molecules from all directions to one side of dA which are incident upon dA, consider that for a given value of θ, $d\omega$ is $2\pi \sin\theta\, d\theta$ whilst θ varies from 0 to $\frac{\pi}{2}$. Therefore, the total number concerned is

$$\frac{n\bar{v}\, dA}{4\pi} \int_0^{\pi/2} 2\pi \sin\theta \cos\theta\, d\theta = \frac{n\bar{v}}{4}\, dA.$$

Hence, the number of molecules striking unit area per second is N, where

$$N = \tfrac{1}{4} n\bar{v} \tag{A16}$$

Put

$$\bar{v} = \sqrt{\frac{8\mathbf{k}T}{\pi m}} = \sqrt{\frac{8\mathbf{R}T}{\pi M}} \text{ from equation (A9),}$$

where M is the molecular weight of the gas concerned, and $n = \frac{p}{\mathbf{k}T} = \frac{p\mathbf{N}}{\mathbf{R}T}$ from equation (A5); then equation (A16) can be expressed in the alternative form:

$$N = \frac{\frac{1}{4}p\mathbf{N}}{\mathbf{R}T}\sqrt{\frac{8\mathbf{R}T}{\pi M}} = \frac{p\mathbf{N}}{\sqrt{2\pi M\mathbf{R}T}} \tag{A17}$$

Substituting $\mathbf{R} = 8{\cdot}314 \times 10^7$ and $\mathbf{N} = 6{\cdot}023 \times 10^{23}$ gives

$$N = \frac{2{\cdot}634 \times 10^{19} p}{\sqrt{MT}}$$

where p is in dyne cm^{-2}, *i.e.* microbar.

Substituting 1 torr = $1{\cdot}333 \times 10^3$ microbar (Table 1.1), gives

$$N = \frac{3{\cdot}5 \times 10^{22} p}{\sqrt{MT}} \tag{A18}$$

where p is in torr.

In the case of **molecular effusion through an aperture** of area A in a thin wall connecting two vessels which are large compared with the maximum aperture dimensions (§ 1.5(*a*)), if p_1 and p_2 are the molecular pressures in the two vessels and $p_1 > p_2$, then the number of molecules traversing the aperture is seen from equation (A17) to be

$$\frac{(p_1 - p_2)\mathbf{N}A}{\sqrt{2\pi M\mathbf{R}T}}.$$

Hence, the throughput $Q = pV = n\mathbf{k}T = n\frac{\mathbf{R}}{\mathbf{N}}T$ is given by

$$Q = \frac{(p_1 - p_2)\mathbf{N}A}{\sqrt{2\pi M\mathbf{R}T}} \cdot \frac{\mathbf{R}T}{\mathbf{N}} = (p_1 - p_2)A\sqrt{\frac{\mathbf{R}T}{2\pi M}}$$

(*see* equation 1.9).

TABLE A1

Physical data for some gases and vapours

Gas	Molecular weight (Chemical scale)	Density in gram/litre at N.T.P.	Boiling point, °C	Critical pressure, atm	Critical tempera-ture, °C	Viscosity at 760 torr and 20° C micropoise	Mean molecular diameter 10^{-8} cm	Mean free path at 10^{-3} torr and 20° C cm	First ionization potential in volts	
									for atom	for molecule
Air	—	1·2928	—	37·2	−140·7	181		5·1	—	—
Ammonia	17·03	0·7710	−33·35	111·5	132·4	98·2	3·02	4·65	—	11·2
Argon	39·944	1·784	−185·7	48	−122	221·7	2·90	5·07	15·68	—
Bromine	159·83	7·139	58·78	131	302	154	—	—	11·8	12·8
Carbon monoxide	28·01	1·250	−190	35	−139	175	3·15	—	—	14·1
Carbon dioxide	44·01	1·977	−78·5	73	31·1	148	3·28	3·34	—	14·4
Chlorine	70·91	3·214	−34·6	76·1	144	132·7	—	3·47	12·95	13·2
Helium	4·003	0·1785	−268·9	2·26	−267·9	194·1	2·30	14·6	24·46	—
Hydrogen	2·016	0·0899	−252·8	12·8	−239·9	87·5	2·36	9·3	13·527	15·6
Krypton	83·70	3·708	−152·9	54	−63	250	3·20	4·05	13·93	—
Mercury vapour	200·61	—	—	—	—	—	3·0	6·3	10·39	—
Neon	20·18	0·9002	−245·9	25·9	−228·7	311·1	—	10·4	21·47	—
Nitrogen	28·02	1·2506	−195·8	33·5	−147·1	176	3·20	5·1	14·48	15·51
Oxygen	32·00	1·429	−182·96	49·7	−118·8	202	2·95	5·4	13·55	12·5
Water vapour	18·016	0·606	100	217·72	374	98	—	3·4	—	12·56
Xenon	131·30	5·851	−107·1	58·2	16·6	226	3·7	3·0	12·08	—

TABLE A2

Vapour pressure of mercury at various temperatures in °C (in torr)

°C	−78	−30	−20	−10	0	10
torr	3×10^{-9}	4.8×10^{-6}	1.8×10^{-5}	6×10^{-4}	1.85×10^{-4}	4.9×10^{-4}

°C	20	40	60	80	100	150	200
torr	1.2×10^{-3}	6×10^{-3}	2.5×10^{-2}	8.9×10^{-2}	2.7×10^{-1}	2·8	17·3

Accommodation coefficient. This term is concerned with the transference of energy to a surface by impinging gas molecules. It is defined as the ratio of the energy actually transferred between incident gas molecules and the surface to the energy which would be transferred if the molecules attained thermal equilibrium with the surface. It is designated by α, where

$$\alpha = \frac{T_r - T_i}{T_s - T_i}$$

where T_i is the temperature of the incident molecules which impinge on a surface at a temperature T_s and these molecules are re-emitted with a temperature T_r.

The **condensation coefficient** is the ratio of the number of molecules which condense on a surface to the number incident on that surface in unit time.

APPENDIX B

DATA RELEVANT TO RESISTANCE AND INDUCTION HEATING

Resistance heated tubular furnace. If a totally enclosed thermally insulated space is to be heated by an energy source inside it, the energy required to maintain it at a given temperature will depend on the quality of insulation around the wall of the space. Very similar considerations will prevail when the space is surrounded by a shell of material which is a good conductor of heat and the source of heat (*e.g.* an electrically insulated winding) is spread evenly around the shell on its outside, the whole being surrounded by heat insulating material, or by effective heat radiation shields.

Consider a cylindrical tube with stoppers at both ends. Let this be heated by an insulated winding on the outside which carries electric current. Near the ends of the tube there will be a drop of temperature. The effective length of the tube is therefore taken as the length between the two cross-sections at which the temperature is not less than 90% of that in central region of the tube. Table B1 then gives the energy consumption in watts per sq cm of heated surface of even temperature in various cases (based on M. Pirani, *Elektrothermie*, Berlin, 1930, p. 210).

Once the total energy requirements are known the power supply has to be decided upon. For vacuum furnaces employing an internal resistance element it is advisable to limit the maximum voltage to 100 V in the hot zone to avoid possible ionization effects which might cause breakdown.

For mechanical reasons, the diameter of the heater wire should not be less than 0·5 mm for temperatures up to 1000° C and 1 mm for higher temperatures. For temperatures above 1600° C, self-supporting heater elements (§ 14.4) are recommended.

In all cases, the calculation of the power supply is based upon the equation:

$$W = EI = I^2R_t = \frac{I^2\rho_t l}{A}$$

where W = total wattage, E = voltage, I = current in amp, R_t = resistance in ohm at required temperature t, ρ_t = resistivity of heater material at temperature t, l = length of heater winding and A is the cross-section area of the heater wire.

Resistance heated bake-out oven. A. I. Bennett [*Vacuum*, 3, p. 43 (1953, published 1954)] gives a rapid graphical procedure for the design of ovens intended for bake-out on vacuum systems at temperatures up to 500° C.

For the oven, let T_i = the inside temperature, T_s = the outside surface

TABLE B1

Approximate energy consumption for tubular laboratory furnaces (in watt per sq cm)

Temperature, °C	Total radiation from a black body, W/cm²[1]	For polished tungsten tube in hydrogen, W/cm²	For carbon grain[5] surface surrounded by 3 cm of ZrO_2 insulation, W/cm²	For 5 tungsten or molybdenum radiation shields $\frac{1}{8}$ in. apart, W/cm²	For ZrO_2 insulating wall 3 cm thick and internal tungsten coil, W/cm²	For insulation in form of 3 cm thickness of kieselguhr,[4] W/cm²	For insulation in form of 5 cm thickness of kieselguhr, W/cm²
500	~2	—	—	—	4	0·6	0·3
1000	15	40	8	4·5	7	1·9	0·8
1250	30	70	12	—	9	2·8	1·5
1500	56	120	20	—	12	3·9[3]	2·5
1600	70	150	22[2]	12	13		
1700	86	180	25	—	14		
1800	104	210	28	16	15		
1900	126	250	33	—	16		
2000	150	300	40	20	18		
2500	333	650	70	36	—		
3000	650	1200	—	60	—		

[1] Calculated from Stéfan–Boltzmann law: $E = \sigma T^4$ where σ = Stéfan's constant = $5{\cdot}67 \times 10^{-12}$ watt cm^{-2} deg^{-4}.

[2] Upper limit for fireclay insulation.

[3] Upper limit for kieselguhr which begins to sinter at 1400° C.

[4] This heat insulation is also achieved by 4 in. thickness of insulating brick, *e.g.* Morgan Crucible Company 'ΔFF', and Derby Silica Brick Corporation, 'Birsil'; up to 1200° C, foamed ciment fondu may be used.

[5] Furnace tube is surrounded by carbon grains about 1 mm in diameter and then by zirconium oxide.

temperature and T_o = the ambient room temperature. The heat loss Q_L per unit area of the outer surface is decided by radiation, conduction and convection and so depends on ε, the emissivity of the outer surface, and on T_s and T_o. If Q_T is the heat transferred through the oven walls per unit area, Q_T depends on the thermal conductance of the wall material and on $T_i - T_s$. The surface temperature, T_s, reaches an equilibrium when $Q_L = Q_T$. T_s can be found graphically if curves are plotted of Q_L and Q_T as functions of T_o, T_s and T_i.

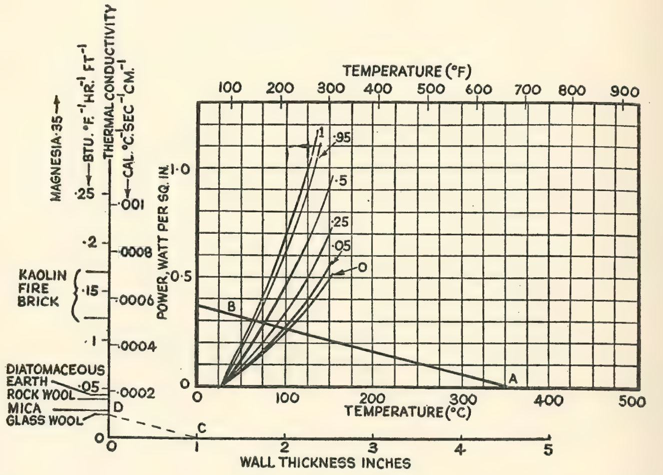

FIG. B1 Chart for rapid graphical design of bake-out ovens (*after Bennett*)

Parameters on curves are emissivities, ε. ε = 0·95 to 1 for fire brick, flat black enamel, asbestos; ε = 0·5 for iron sheet and light oxide; ε = 0·25 for galvanized iron; ε = 0·05 for aluminium

Figure B1 is a family of curves with the emissivity ε of the material as the parameter showing the power loss in watt/sq in of surface due to combined radiation, conduction and convection plotted against the surface temperature where the ambient room temperature is 25° C. These curves are thus graphs of Q_L against T_s. On this figure is also given axes showing the oven wall thickness in inches and the thermal conductivities of various insulating materials in the units cal.°C^{-1} sec^{-1} cm^{-1} and also B.t.u. °F^{-1} hr^{-1} ft^{-1}. For a required inside temperature T_i a straight line AB is drawn through the point T_i on the temperature axis and with a slope equal to the negative of the thermal conductance of the oven wall. This line AB will be a graph of Q_T against T_s for the given value of T_i (assuming that the thermal conductivity of the wall material is independent of the temperature). The intersection of AB with the appropriate curve of Q_L against T_s will give the operating surface temperature T_s and the surface power loss per square inch. The required slope of the line AB is simply the thermal conductivity of the wall insulating material divided by its thickness.

Bennet gives the following example: an oven is to be designed to attain an inside temperature of 350° C. The wall thickness is 1 in., the insulating material is Pyrex glass wool, the outer surface is aluminium sheet of emissivity about 0·05 and the surface area is 4000 sq in.

To find the required heating power and the outer surface operating temperature, the straight line CD is drawn from the point 1 in. on the thickness scale to the point on the thermal conductivity scale corresponding to the value for Pyrex glass wool. The line AB is then drawn parallel to CD such that it intersects the temperature axis at the required inside temperature of 350° C. The point of intersection of AB with the curve of Q_L against T_s for an emissivity of 0·05 (*i.e.* for aluminium) has the co-ordinates 0·26 watt/in^2 and 98° C. The required power input is therefore the oven surface area times 0·26, *i.e.* 4000 × 0·26 = 1040 watt and the surface temperature will be 98° C. In practice, a correction will be necessary for any supporting struts or members between the inner and outer shells within which the glass wool is packed.

In general, it is necessary to provide to the oven or furnace during the heating-up period a larger power than that calculated for operation at the final temperature to prevent unduly long warm-up times.

Induction heating. The practice is to place a coil (usually water-cooled) carrying alternating current at a frequency of f c/s around the conductor to be heated so as to induce in this conductor eddy-currents which raise its temperature. Equations are given by K. Reche [*Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern*, **12**, pp. 1 to 33 (1933)] which enable the effective power absorbed by the conductor to be calculated in the case where this conductor is a solid cylinder surrounded by a coaxial coil. These equations apply to the practical cases of a cylindrical crucible of insulating material containing a metal charge which is surrounded by the coil in vacuum, as in a vacuum induction furnace, and to the induction heating of a solid cylinder of metal within a vacuum tube with the coil in air around the glass envelope. In this second case, the usual requirement is to heat an anode or other vacuum tube electrode in the form of a hollow cylinder. If the wall thickness of this hollow cylinder is greater than the depth of penetration of the alternating field (which is likely to be the case for high frequency working, *see* Fig. B3) then the equation for the power absorbed still applies.

Reche's equations are:

$$W_E = 2{\cdot}81 \times 10^{-6}\, G\sqrt{f\rho}\, N^2I^2 \tag{B1}$$

$$W_L = \frac{1{\cdot}65 \times 10^{-6}}{\rho_L}\,\frac{R_c}{h}\sqrt{\frac{f}{F_w}}\,N^2I^2 \tag{B2}$$

$$W_F = W_c + W_{ch} \tag{B3}$$

$$W_c = \frac{-2{\cdot}5 \times 10^{-8} f R_c^2 N^2 I^2}{h + 0{\cdot}9\, G_1} \tag{B4}$$

$$W_{ch} = 7{\cdot}9 \times 10^{-9} f B R_{ch} N^2 I^2 \tag{B5}$$

where W_E = effective power dissipated in the charge or cylinder
W_L = power loss in the coil
W_c = reactive ('wattless') power in coil alone
W_{ch} = reactive power in charge or cylinder
W_F = reactive power in furnace;

these powers being given in watts, and

f = frequency of a.c. through induction coil in c/s
ρ = resistivity in ohm-cm of material of charge or cylinder at the temperature attained
ρ_L = resistivity in ohm-cm of material of coil
N = number of turns of induction coil
I = r.m.s. current through induction coil
R_c = radius of induction coil
R_{ch} = radius of charge or cylinder
h = height of induction coil
d = outside diameter of tubing of induction coil

$$F_w = \frac{\pi dN}{4h} \qquad \text{(B6)}$$

If V is the r.m.s. voltage across the induction coil, VI is the apparent power and $VI \cos \phi$ the real power where $\cos \phi$ is the power factor. Note that:

$$(W_E + W_L)^2 + W_F{}^2 = W_A = VI \qquad \text{(B7)}$$

where W_A is the apparent power consumed by the induction heater; also

$$W_A \cos \phi = W_E + W_L.$$

The factors G and B in equations (B1) and (B5), respectively, are both functions of R_c/R_{ch} and R_{ch}/h and are obtained from the graphs of Fig. B2.

In the case of a solid cylinder or charge, the value of R_{ch}, the radius of the charge or cylinder, is the actual geometrical radius minus 0·75 times the depth of penetration of the r.f. current into the charge. This depth, δ, is given for copper at 290° C and liquid iron at 1600° C as a function of the frequency of the a.c. in Fig. B3 [after W. Esmarch, *Siemens Z.* **17**, p. 271 (1937)].

To calculate the electrical requirements of an induction heater, the first step is to estimate the necessary value of W_E. When the charge or the metal cylinder is raised to a temperature T° abs. it will radiate energy at a rate W_R given by

$$W_R = 5{\cdot}67 \times 10^{-12}\, T^4 A \text{ watt} \qquad \text{(B8)}$$

assuming it is a black-body, where A is its surface area. This should be multiplied by ε, the emissivity of the surface, if it is known.

For a solid metal cylinder or a hollow cylinder of wall thickness greater than the depth of penetration of the a.c. field, the necessary equation for the calculation of NI, the ampère-turns of the induction coil, is then obtained simply by equating the power absorbed, W_E, from equation (B1) to the power radiated, W_R, from equation (B8). Therefore,

$$2{\cdot}81 \times 10^{-6}\, G\sqrt{f\rho}\, N^2 I^2 = 5{\cdot}67 \times 10^{-12}\, T^4 A.$$

$$\therefore \quad NI = \sqrt{\frac{2 \times 10^{-6}\, T^4 A}{G f^{\frac{1}{2}} \rho^{\frac{1}{2}}}}$$

NI is therefore given once the required temperature T is decided, ρ is known and G is determined from Fig. B2 in relation to the geometry of the cylinder and coil.

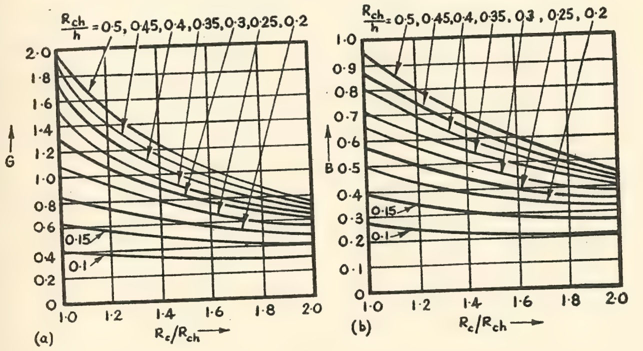

FIG. B2

(*a*) Evaluation of the factor *G*
(*b*) Evaluation of factor *B*

For the induction heating of electrodes in vacuum tubes, the frequency of the a.c. is usually chosen to be in the range 10^5 to 10^6 c/s, and the current is supplied by a valve oscillator (*see* § 6.4).

For the melting of a metal in a vacuum induction furnace lower frequencies in the audio range are employed (*see* § 14.2) where the power is provided by a motor generator set. To reduce electrical losses, the induction coil is tuned to resonance with the generator frequency by a bank of capacitors. To prevent metal structures within the vacuum furnace from being heated to dangerously high temperatures in the alternating field, a rule of thumb practice is to keep any large structures, such as the bottom of the crucible support on the base of the vacuum tank and the tank walls themselves, at a distance from the induction coil of at least 1·5 times the diameter of this coil. The losses will then be only 0·1 to 0·2% of the total energy absorbed by the charge. Thus, if 50 lb of steel are melted by a power input of 20 kW at a frequency of 3000 c/s, the tank will only absorb 20 to 40 W. Of course, the tank walls would absorb a much greater quantity of heat due to radiation from the heated charge but this is taken care of by water cooling.

Small metal parts like screws and bolts within the vacuum furnace are best made of stainless steel and kept at distances exceeding $\frac{3}{8}$ in. at 2000 c/s and $\frac{3}{16}$ in. at 10,000 c/s. Closed loops of metal within the alternating field cannot be tolerated.

As an example of vacuum induction melting practice, suppose about 3500 cc of an alloy melting at about 1550° C are to be melted in 30 min and kept at 1600° C for some time after melting. The density of the alloy is 7 gram/cm³. A crucible of sillimanite is used of inside dia 16 cm and outside dia 18·5 cm approx and of height 35 cm. It is surrounded by a sillimanite ramming of about 2 cm thickness and the bottom of the crucible is 4 cm thick. The alloy will occupy about half the volume of the crucible and thus will form a cylinder of height about 18 cm and dia 16 cm. The theoretically evaluated thermal capacity including the latent heat of fusion is found to be 300 calories per gram (appropriate thermal constants are obtained from, *e.g.*, *The Handbook of Chemistry and Physics*, Chemical Rubber Publishing Company, Cleveland, Ohio, U.S.A., or *Tables of Physical and Chemical Constants*, by G. W. C. Kaye and T. H. Laby, Longmans, Green and Company, London). This will mean that a power input of 18 kW is necessary if the melting is to be completed in 30 min, assuming no heat losses. In order to keep the melt at the temperature of 1600° C, about 15 watt/cm² will be needed for that part of the melt which is in contact with the walls and the bottom of the crucible, (compare the figure of 13 watt/cm² at 1600° C for 3 cm of ZrO_2 given in Table B1). On multiplication by the area of contact, a value of about 16·5 kW is obtained. To this must be added the radiation from the surface of the molten metal. Using equation (B8) and multiplying by a factor of 0·6 to account approximately for the departure from black-body radiation conditions, this radiation is found to be about 40 watt/cm²; hence, for the surface area concerned, it amounts to 8 kW approx. The input power required to maintain the melt at 1600° C is therefore 24·5 kW. This is greater than the power of 18 kW needed to bring about melting in the maximum desired time of 7 min. A power of 25 kW will therefore satisfy both conditions and this is the value of W_E which is used in equation (B1) to calculate the necessary ampere-turns of the induction coil, *i.e.* NI.

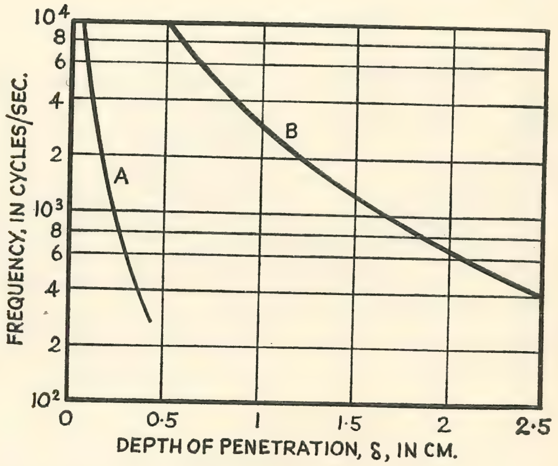

FIG. B3 Plot of depth of penetration of current against frequency: curve A, for copper at 20° C and curve B, for liquid iron at 1600° C

Equation is $\delta = 5000\sqrt{\frac{\rho}{f}}$, where ρ is specific resistance in ohm-cm, f is frequency in c/s, and δ = depth of penetration in cm. Magnetic permeability of material is assumed to be unity in c.g.s. system of units

The apparent power of the induction heater is then $W_A = VI$, given by equation (B7) where W_L is calculated from equation (B2) and W_F from equation (B3). To evaluate equation (B2), the factor F_w is needed; this can be taken to be 0·8 with a sufficiently close approximation, or calculated from equation (B6) provided that N is known, *i.e.* the current I has been decided. In arriving at a suitable value for I, it must be borne in mind that, normally, the voltage V across the coil should not exceed 250 V because of the risk of breakdown by arcing when sudden eruptions of gas take place from the melt.

Thermocouples are generally used for the measurement of the temperature in vacuum furnaces. For temperatures up to 700° C (continuous reading) or 1300° C (spot reading) a Chromel–Alumel couple is suitable. For the range from 1250° to 2600° C, a tungsten–molybdenum couple may be used; below 1250° C, the e.m.f. of this couple changes sign. A graphite–tungsten couple is useful up to 1650° C. Noble metals are preferable for thermocouples where high precision is necessary, *e.g.* 40% rhodium–platinum against 20% rhodium/platinum, up to 1900° C.

In the use of thermocouples the following precautions are important:

(*i*) Measurement and control of the cold junction.

(*ii*) Removal of the cold junction to as far as possible away from the furnace; compensating leads must be used.

(*iii*) Insulation leaks must be avoided: *e.g.* alternating current may leak into the thermocouple from the a.c. mains through the protecting sheath and it may become rectified and so produce a false reading.

(*iv*) Screening of the thermocouple leads from a.c. pick-up is sometimes necessary.

(*v*) For accurate measurements, a potentiometer should be used to determine the thermocouple e.m.f. Direct reading meters should be calibrated at the ambient temperature and should have a high resistance compared with the thermocouple wires. If the meter resistance is R and that of the thermocouple plus leads is r, a correction of $\frac{100r}{R}\%$ should be added to the meter reading. Thus, for a Chromel–Alumel couple made of 26 s.w.g. wires (the smallest gauge recommended) a length of about 3 ft will have a resistance of 3 ohm approx. With a 300 ohm meter, the correction is then 1%.

(*vi*) Errors due to contamination of the thermocouple should be avoided by the use of tight sheaths (which, of course, delay the response). Morgan Crucible Company ΔH, a mullite type material, is recommended for temperatures up to 1500° C.

(*vii*) The thermocouple is best calibrated at the site where it will be used in practice.

For further data *see* British Standards Institution, *Temperature Code*, B.S. No. 1041: 1943, and J. A. Hall, *Practical Thermometry* (Institute of Physics, London, 1953).

APPENDIX C

THERMIONIC CATHODES

Pure metallic emitters. The electron emission from a heated pure metal in vacuum is determined by the Richardson–Dushman equation:

$$I = A(1 - r)T^2\, e^{\frac{-\phi}{kT}}$$

where I is the saturated emission current in amp cm^{-2}, A is theoretically 120 amp cm^{-2} deg^{-2}, r is the reflection coefficient for electrons of the emitting surface, T is the absolute temperature (°K), **k** is Boltzmann's constant and ϕ is the thermionic work function. If ϕ is given in electron-volt, then $1/\mathbf{k} = 11{,}606$ deg/eV. The values of ϕ and $A(1 - r)$ for some pure metals are given in Table C1.

TABLE C1

Values of $A(1 - r)$ and ϕ in the Richardson–Dushman equation

Metal	$A(1 - r)$ amp cm^{-2} deg^{-2}	Thermionic work function ϕ eV	Metal	$A(1 - r)$ amp cm^{-2} deg^{-2}	Thermionic work function ϕ eV
Barium	—	2·11	Nickel	30	4·60
Caesium	162	1·81	Platinum	32	5·32
Calcium	—	2·24	Rhenium	52	4·80
Carbon	30	4·34	Rhodium	33	4·80
Chromium	48	4·60	Tantalum	60	4·12
Cobalt	41	4·41	Thorium	70	3·38
Columbium	—	3·96	Titanium	—	3·95
Iron	26	4·48	Tungsten	72	4·52
Molybdenum	55	4·20			

Of the pure metals, tungsten, tantalum, columbium (*i.e.* niobium) and rhenium have been most used as thermionic cathodes in the form of directly heated filaments and, of the four, tungsten is used much more extensively than the others.

The thermionic emission from pure tungsten (melting point: 3370° C) in mA cm^{-2} is $1{\cdot}5 \times 10^{-10}$ at 830° C, $2{\cdot}3 \times 10^{-1}$ at 1630° C, 298 at 2230° C and 1000 at 2350° C. The life is limited by evaporation of the metal on heating (*see* Fig. 14.21) but is about 6000 hours for wire of 0·25 mm dia at the usual operating temperature of 2227° C (*i.e.* 2500° K). The life will, however, decrease with wire diameter to only about 800 hours for 0·1 mm and about 150 hours for 0·05 mm.

Tungsten can be cleaned effectively by pre-heating the filament in vacuum; alternatively, a number of filament assemblies may be mounted in oxidized stainless steel jigs or clamps or on mandrels and hydrogen-stoved at 900° C for 20 to 30 min (*M.I.T. Tube Laboratory Manual*). Such pre-heating renders the tungsten brittle.

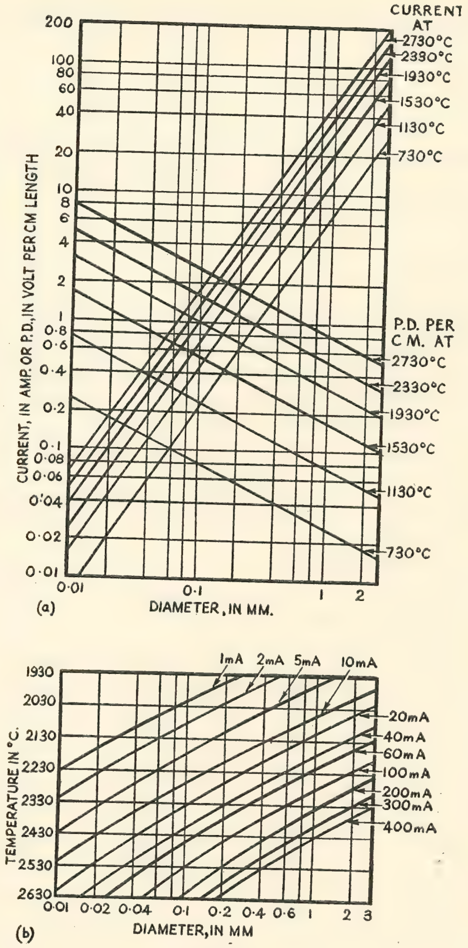

FIG. C1

(*a*) For tungsten wires of various diameters, the p.d. per cm length and the current at various temperatures

(*b*) For tungsten wires of various diameters, the emission per cm length at various temperatures

Fig. C.1(*a*) gives for tungsten wire of circular cross-section and of various diameters the potential difference across 1 cm length of the wire for various temperatures and the current required for various temperatures (Espe and Knoll, *Werkstoffkunde der Hochvakuumtechnik*, Springer, 1936); Fig. C.1(*b*) gives the emission in mA per cm length of tungsten wire for various diameters and temperatures (Steyskal, S9).

Filamentary cathodes of tungsten of straight, hairpin, flat spiral and ribbon forms are used in high voltage (> 2500 V) electron tubes such as vacuum and gas-filled rectifiers, power valves and X-ray tubes because they resist (as compared with oxide-coated cathodes) disintegration by high energy positive ions. As tungsten can be readily cleaned and degassed by heating in vacuum and as it can be repeatedly cooled and air admitted to the vacuum chamber without damage to its emission properties, it is a usual choice for a directly heated thermionic cathode in demountable vacuum systems and plants.

Tantalum (melting point 3027° C) and columbium (melting point 1950° C) are alternatives to tungsten and have the advantages that they are more readily formed and welded and provide greater emission at a given temperature (compare the work functions given in Table C.1). However, whereas tungsten may be heated to 2230° C (vapour pressure = 10^{-7} torr), columbium cannot be used at this temperature; on the other hand, tantalum would give the same electron emission at about 2030° C and have a vapour pressure of about the same magnitude. Compared with tungsten, however, tantalum sorbs gas readily when heated (§ 6.13).

Recently, filamentary thermionic cathodes of rhenium (melting point 3180° C; vapour pressure at 2200° C = 10^{-6} torr) have proved to be of interest because of its following advantages compared with tungsten: it is stronger after heating; when heated it does not form stable nitrides, or react appreciably with water vapour; its greater electrical resistivity enables larger diameter, more rugged filaments to be used with the same supply e.m.f. Hall (H9) chooses a rhenium filament (§ 3.9) for the hot-cathode of an ionization gauge used to measure the pressure in a maser containing ammonia. A full account of the properties of rhenium and of tungsten–rhenium and molybdenum–rhenium alloys is given by Sims, C. T., and Gaines, G. B., 'Rhenium for electron tubes', *Proceedings of the Fourth National Conference on Tube Techniques*, p. 161, (New York University Press, 1959).

Thoriated tungsten filamentary cathodes. Greater efficiency than for a pure metal may be obtained by the use of thoriated tungsten. Whereas the emission per cm² from tungsten at 2230° C is 4 mA/watt, for thoriated tungsten at the normal operating temperature of 1600° C, the efficiency can be as much as 100 mA/watt. The work function of thoriated tungsten is 2·6 eV.

The basic material is tungsten wire containing 1 to 2% thorium oxide. The mounted filament in the electron tube is heated in vacuum to 2500° C for about one minute. This causes reduction of the thorium oxide to thorium ($ThO_2 + W \rightarrow Th + WO_2$). The temperature is then reduced to an activation temperature of 1700 to 2000° C which is maintained for some minutes. During this activation, thorium migrates to the surface of the tungsten; some of it evaporates but sufficient remains in the form of an electropositive ionic layer at the surface. The final operating temperature is 1500° to 1600° C. To improve the emission, naphthalene vapour may be admitted at the operating temperature to form a layer of tungsten carbide at the filament surface which results in stronger binding (and so less evaporation) of the thorium. Adequate 'carbonization' of the filament is indicated by an increase of the filament resistance by about 15%. The gases from the naphthalene vapour are subsequently pumped away.

Thoriated tungsten filaments are used in medium power tubes. They can also be employed in hot cathode ionization gauges and other ion sources. Though attractive for use in demountable vacuum systems because of their greater emission per watt than tungsten, the filament must be re-activated after admitting air and re-pumping; success is often elusive unless the filament is replaced frequently.

Oxide-coated cathodes. By far the majority of small and medium size electron tubes employ directly or indirectly heated cathodes consisting of a mixture of barium and strontium oxides on a base of nickel or nickel alloy. As these oxides are hygroscopic, the cathode coating material is made up from the non-hygroscopic barium and strontium carbonates (about 60% $BaCO_3$, 40% $SrCO_3$ and some 0·5% $CaCO_3$) in the form of a suspension (particle size 6 to 12 micron) in a binder usually composed of nitrocellulose and alcohol. (The M.I.T. Tube Laboratory Manual recommends a binder consisting of nitrocellulose in equal parts of butyl alcohol and acetate to give a viscosity of 17·5 centipoise at 23° C; to 1700 cc of this binder is added 1600 gram of a mixture of 57·3% $BaCO_3$, 42·2% $SrCO_3$ and 0·5% $CaCO_3$; after ball-milling for 7 hours, the suspension is diluted with 750 cc of the binder). Usually, the cathode material suspension is sprayed on to the cathode by means of a compressed air (or nitrogen) gun. Alternatively, cathode coatings may be prepared by dipping, painting, or cataphoretically.

The oxide-coated cathode is assembled within the electron tube and is then processed during the exhaust schedule. A typical schedule for a single tube is as follows:

For a small electron tube, *e.g.* radio receiver valve: (*a*) the tube is sealed on to the pumps and exhausted to 10^{-5} to 10^{-6} torr by a diffusion/rotary pump combination (rotary pumps only are sometimes used in mass production schedules, in which case the pressure is about 10^{-3} torr); (*b*) bake-out for 10 min at 450° C; (*c*) induction-heat the electrodes for 20 to 100 sec, depending on the size of the anode; (*d*) switch on the filament or cathode heater with about 1½ times the normal voltage across it (*i.e.* about twice the normal wattage) so that it is over-run at a temperature of about 1100° C, and maintain this temperature for a time of 10 to 100 sec depending on the size of the cathode (the optimum cathode heating time can only be found by trial); during this period, the carbonates are reduced to oxides and carbon dioxide and monoxide are evolved and pumped away; (*e*) reduce the cathode voltage to the normal operating value and induction-heat the electrodes again so that the cathode and electrodes are simultaneously hot and gas cannot be interchanged between them; (*f*) stop induction-heating and flash the getter; (*g*) seal off immediately. In production schedules, the getter is sometimes flashed after seal-off.

The tube, sealed from the pumps, is then subjected to an activation schedule on an 'ageing' rack. The cathode is run at about 900° C and current is drawn to the other electrodes for 2 to 5 min with all these electrodes strapped together and maintained at a positive potential. The tube is then run for a further 30 min with the electrodes at normal operating potentials.

The effective work function of a correctly processed oxide-coated cathode is about 1 eV. An indirectly-heated cathode of the 8 watt class should give a total emission (saturation potential applied momentarily to grids and anode strapped together) of about 500 mA at the normal operating temperature of 1050° K (777° C). A temperature range from 750° to 850° C is permissible for normal operation, *i.e.* about 5·4 to 7·5 V for a nominally 6·3 V heater. These cathodes will give a maximum emission of 1 amp/cm² but a tenth of this is recommended for long life in normal operation; under short duration pulse conditions, as much as 50 amp/cm² of emission may be obtained momentarily.

The cathode core or base metal is usually of nickel containing a small quantity of a reducing agent, *e.g.* 0·05% of magnesium, aluminium, silicon or even tungsten, to ensure satisfactory processing of the cathode to an efficient level of emission. The reduction action of this addition is, *e.g.*, $Mg + BaO \rightarrow MgO + Ba$. The use of silicon for this purpose has recently been deprecated because the formation of silica leads to unduly high cathode interface resistance.

An activated oxide-coated cathode is readily poisoned by the action of oxygen, chlorine, sulphur or water vapour. These cathodes are therefore unsuitable for demountable vacuum tubes unless they are replaced frequently and re-activated each time air is admitted. Exposure of the heated cathode to hydrogen or methane at a pressure of about 10^{-2} torr may help to restore its emission if it has become poisoned.

The standard work on oxide-coated cathodes is: Herrman, G., and Wagener, S., *The oxide-coated cathode* (Chapman and Hall Ltd., London, 1951). More recent data is given in *Enlarged abstracts of papers read at the Spring meeting in Philadelphia*, May 1959, published by the Electrochemical Society, Electronics Division.

Dispenser cathodes. On a standard oxide-coated cathode, the barium forms a surface layer about 5×10^{-7} cm thick, weighing about 5×10^{-6} g cm^{-2}. About ten such layers are lost by evaporation in 1000 hours with a cathode temperature of 1000° C (higher than the usual operating temperature of 800° C). During the life of a cathode, barium must be replaced by diffusion to the surface from the body of the cathode coating. To provide enhanced emission, rugged construction, insensitivity to positive ion bombardment and the ability to provide large currents in specialized tubes such as large gas-filled triodes (thyratrons) and magnetrons, the *dispenser cathode* has been developed. To make up the loss of emitting material by evaporation, this material is continually dispensed to the surface from a supply source. In this respect, the normal oxide-coated cathode might be considered as a dispenser type, because barium is made available from within the cathode coating, but it is not usually classed as such. On the other hand, the thoriated tungsten cathode is certainly a type of dispenser cathode; indeed, developments of it have led to its use in, for example, magnetron tubes.

Types of dispenser cathode are:

(*i*) The cathode is of tungsten which is heated in an atmosphere of an alkali metal (caesium, potassium or rubidium). As these metals have first ionization potentials less than the work function of tungsten, they readily form electron emitting monolayers on the tungsten surface. The rate of arrival of the alkali metal at the cathode surface depends on its vapour pressure and so on the temperature.

(*ii*) A. W. Hull (*Phys. Rev.*, **56**, p. 86, 1939) introduced the first dispenser cathode, intended for use in a large thyratron. A coiled evaporator loaded with barium aluminate is heated to 1150° to 1200° C to evaporate barium on to the cathode surface consisting of fins of tungsten or molybdenum heated to 850° C. This cathode provides reliably an emission current density of 1 amp cm^{-2} at 730° C, but it has not been used extensively.

(*iii*) The L-cathode consists essentially of a cavity within the cathode itself containing a barium–strontium oxide mixture. This cavity is separated from the cathode surface by a porous wall of sintered tungsten powder. The oxides within the cavity are heated by an insulated filament within a molybdenum housing so that barium and barium oxide diffuse through the sintered tungsten to the cathode surface. At this surface, the provision of an adsorbed layer of barium ions forms an efficient electron emitter at an operating temperature of 900° to 1300° C. A current density of 30 amp cm^{-2} is possible at a temperature of 1250° C with a life of 100 hours.

(*iv*) A barium–nickel cathode made by subjecting a finely divided mixture of 70% by weight nickel powder with 30% barium–strontium carbonates to a pressure of 50 to 100 tons per sq in. To accelerate the production of barium metal, an activating agent such as boron, tungsten, titanium or zirconium may be added to the mixture. At 1000° C, 1 amp cm^{-2} is provided for 5000 hours whilst 3 amp cm^{-2} is possible at 1070° C for 2000 hours.

(*v*) A matrix cathode, used in magnetrons, consisting of a nickel tube on which is sintered a nickel powder impregnated with barium–strontium oxides. The barium diffuses to the surface from the depth of the coating.

(*vi*) An impregnated and pressed cathode consisting of 2·5 $Ba.Al_2O_3$, 0·5 CaO in tungsten. On heating, free barium is produced which migrates through the pores of the tungsten. Cathodes of this type have long life and provide 2 amp cm^{-2}.

(*vii*) Lanthanum boride (LaB_6) cathodes. On heating this conducting material to 1500° to 1600° C, lanthanum from the crystal lattice reaches the surface to form a monatomic layer with an emission of 3 to 7 amp cm^{-2}.

(*viii*) Zirconium carbide deposited as a paste or cataphoretically on tungsten wire. At 1500° to 1700° C, an emission of 0·8 amp cm^{-2} is possible.

The pressed and sintered powder artefact cathodes and impregnated cathodes are described more fully by Venema, A., Hughes, R. C., Coppola, P. P., and Levi, R., in *Philips Technische Rundschau*, **19**, p. 281–295 (1957/8). V. L. Stout surveys the mode of operation of most types in 'Dispenser cathodes', *Proceedings of the Fourth National Conference on Tube Techniques*, (New York University Press, 1959). Brief details are also given by Steyskal (S9).

APPENDIX D

MANUFACTURERS OF VACUUM EQUIPMENT

In this list the names of those manufacturers who supply a range of vacuum equipment are marked with an asterisk. In the case of other firms which produce certain specialized apparatus valuable in vacuum technology, the products concerned are noted in brackets. Only the name and address of the principal manufacturing concern is given and not those of agents in other towns and countries.

*Associated Electrical Industries (Manchester) Ltd., Instrumentation Division, (Formerly Metropolitan-Vickers Electrical Co., Ltd.), Trafford Park, Manchester 17, England.
Atlas-Werke A.G., Department Mat., Bremen, Germany (Membrane manometers, vacuum valves, cold-traps, mass spectrometers for leak detection).
Beach-Russ Co., 420, Lexington Avenue, New York 17, U.S.A. (Mechanical rotary pumps).
Beckman Instruments Inc., 2500 Fullerton Road, Fullerton 1, California, U.S.A. (Mass spectrometers).
A. le Boeuf et fils, 194 Rue des Gros-Grès, Colombes, France (Ionization gauges).
Celtiques, 107, Av. du Président, Montreuil (Seine), France (Vacuum pumps, valves).
*Central Scientific Co., 1700, Irving Park Road, Chicago 13, Illinois, U.S.A.
Chapman Valve Manufacturing Co., Essex Street, Indian Orchard, Massachusetts, U.S.A. (Vacuum isolation valves).
Compagnie Générale de T.S.F., 55, Rue Greffulhe, Levallois-Perret (Seine), France (Ionization gauges).
*Compagnie Générale de Radiologie, Department Vide, 48 to 50 Boulevard Galliéni, Issy-les-Moulineaux, Seine, France.
*Consolidated Electrodynamics Corp., Rochester Division, Rochester 3, New York, U.S.A.
Degussa Wolfgang Industrieofenbau, Wolfgang bei Hanau, Main, Germany (Vacuum furnaces).
*Deutsche Vakuumapparate, Dreyer und Holland-Merten G.m.b.H., Sangerhausen, East Germany.
Dupree Swift and Co., Ltd., 23–25, Broadwall, Stamford Street, London, S.E.1, England (Dewar flasks).

*Edwards High Vacuum Ltd., Manor Royal, Crawley, Sussex, England.
Electrothermal Engineering Ltd., 270, Neville Road, London, E.7, England (Heating mantles and tapes).
*Établissements Beaudouin, 1 et 3, Rue Rataud, Paris, 5^{e}, France.
Établissements P. Piel, 48, Rue du Faubourg, Saint Denis, Paris 10, France (Mechanical rotary pumps).
Ferranti Ltd., Hollinwood, Lancs., England ('Tesvac' coil, ion pumps).
General Engineering Co. (Radcliffe) Ltd., Station Works, Bury Road, Radcliffe, Lancs., England (Mechanical rotary pumps).
*Genevac Ltd., [a subsidiary of General Engineering Co. (Radcliffe) Ltd.], Pioneer Mill, Radcliffe, Lancs., England.
*Geraetebau-Anstalt Balzers, Liechtenstein.
Granville-Phillips Co., P.O. Box V-198, Pullman, Washington, U.S.A. (Ultra-high vacuum valves).
Hastings-Raydist Inc., Hampton, 10, Virginia, U.S.A. (Vacuum gauges).
*W. C. Heraeus G.m.b.H., Abteilung Hochvakuum, Hanau, Germany.
Hilliard Corp., 211, W. Fourth St., Elmira, New York, U.S.A. (Oil purifiers for rotary pumps).
Jenaer Glaswerk Schott and Gen., 10, Hattenbergstrasse, Mainz, West Germany (Glass oil diffusion and ejector pumps; glass accessories).
E. Kammerer, 40, Bergstrasse, Bergisch Gladbach, Germany (Mercury manometers and McLeod gauges of the Kammerer type).
Kemet Co., (a division of Union Carbide and Chemical Corp.), Madison Avenue and W. 117th Street, Cleveland, Ohio, U.S.A. (Getters).
Kestner Evaporator and Engineering Co., Ltd., 5, Grosvenor Gardens, London, S.W.1, England (Drying towers).
Kinney Manufacturing Division, The New York Air Brake Co., 3522F Washington Street, Boston 30, Massachusetts, U.S.A. (Mechanical rotary pumps).
Klein, Schanzlin and Becker A.G., Frankenthal, Germany (Piston pumps, water-ring pumps).
*Laboratoire des Basses Pressions, 87, Rue A.G. Bélin, Argenteuil, France.
*Leybold–Elliott Ltd., Elstree Way, Boreham Wood, Herts, England.
*E. Leybold's Nachfolger, also Leybold Hochvakuum Anlagen, 504, Bonnerstrasse, Cologne-Bayental, Germany.
Maschinenfabrik Burkhardt A. G., Basle, Switzerland (Mechanical rotary pumps, water-ring pumps, vacuum driers).
*Micafil S. A., Zürich, Switzerland.
Mirrlees Watson Co., Ltd., Scotland Street, Glasgow, C.5, Scotland (Steam ejector pumps).
Mullard Ltd., Materials Division, Mullard House, Torrington Place, London, W.C.1, England (Ionization gauges, small glass getter-ion pumps, ultra-high vacuum valves).
Murex Ltd., Powder metallurgy division, Rainham, Essex (Vacuum resistance furnaces).

*National Research Corp., Vacuum Engineering Division, 70, Memorial Drive, Cambridge 42, Massachusetts, U.S.A., *also* NRC Equipment Corp., 160, Charlemont Street, Newton Highlands 61, Massachusetts, U.S.A.
*N.G.N. Electrical Ltd., Avenue Parade, Accrington, England.
*Officine Galileo, Florence, Italy.
*A. Pfeiffer G.m.b.H., 31, Bergstrasse, Wetzlar, Lahn, Germany.
C. Pfister S. A., Secfroid, Lausanne, Switzerland (Vacuum drying).
Philips Gloeilampenfabrieken, Eindhoven, Holland (Vacuum gauge tubes; gas liquefying machines).
*Pulsometer Engineering Co., Ltd., Nine Elms Iron Works, Reading, Berks., England.
W. G. Pye and Co., Ltd., Granta Works, Cambridge, England (Pirani-ionization gauge combination).
Radio Corporation of America, Electron Tube Division, 415, S. Fifth St., Harrison, New York, U.S.A. (Vacuum gauge tubes).
Saunders Valve Co., Ltd., Diaphragm Valve Division, Cwmbran, Monmouthshire, Wales (Saunders valves).
Siemens Edison Swan Ltd., 155, Charing Cross Road, London, W.C.2., England (Vacuum gauge tubes; glass-to-metal seals).
Società Apparecchi Elettrici e Scientifici, 215, Via Gallarate, Milan, Italy (Getters).
G. Springham and Co., Harlow New Town, Essex, England (Glass stopcocks).
*F. J. Stokes Corp., 5500, Tabor Road, Philadelphia 20, U.S.A.
Sunvic Controls Ltd., No. 1 Factory Eastern Industrial Estate, Harlow, Essex, England (Hot wire vacuum switches).
Superior Air Products Co., 132, Malvern Street, Newark 5, New Jersey, U.S.A. (Dewar flasks).
Townson and Mercer Ltd., Beddington Lane, Croydon, Surrey, England (Vacuum ovens).
Ultek Corp., 920 Commercial Street, Palo Alto, California, U.S.A. (Ion pumps).
Vacuum Applied, 290, Rue de Chareton, Paris, 12^{e}, France.
*Vacuum Industrial Applications Ltd., Netherton Road, Wishaw, Lanarkshire, Scotland.
Vacuum Metallurgical Developments Ltd., Shelford, Cambridge, England (Vacuum furnaces, vacuum valves).
*Vacuum Research (Cambridge) Ltd., Quayside, Bridge Street, Cambridge, England (Vacuum deposition apparatus, vacuum furnaces).
Vacuum Research Co., 420, Market Street, San Francisco 11, California, U.S.A. (Vacuum valves).
Varian Associates, Palo Alto 26, California, U.S.A. (VacIon pumps).
*W. M. Welch Scientific Co., 1515, Sedgwick Street, Dept. VA, Chicago 10, Illinois, U.S.A.
Wild-Barfield Electric Furnaces Ltd., Elecfurn Works, Otterspool Way, Watford By-pass, Watford, Herts., England (Vacuum furnaces).

MANUFACTURERS OF SPECIAL MATERIALS

The list is concerned with manufacturers of specialized materials used in vacuum technology to which reference has been made in the text.

American Lava Corp., 219, Kruesi Building, Chattanooga 5, Tennessee, U.S.A.
G. Angus and Co., Ltd., Oil Seal Division, Coast Road, Wallsend, Northumberland (Gaco seals).
Associated Electrical Industries (Rugby) Ltd., (Formerly British Thomson Houston Co., Ltd.), Rugby, England.
Baker and Co., 113 Astor Street, Newark, New Jersey, U.S.A.
Bell's Asbestos and Engineering Co., Ltd., Bestabell House, 6–8, Upper Thames Street, London, E.C.4, England.
Bergen Wire Rope Co., 1234, Gregg Street, Lodi, New Jersey, U.S.A.
J. G. Biddle Co., 1316, Arch Street, Philadelphia 7, U.S.A.
British Aluminium Co., Ltd., Norfolk House, St. James's Sq., London, S.W.1, England.
British Drug Houses Ltd., Poole, Dorset, England.
British Oxygen Gases Ltd., East Lane, Wembley, Middx., England.
W. Canning and Co., Ltd., Great Hampton Street, Birmingham 18, England.
Carrs Paints Ltd., Artillery Street, Birmingham 9, England.
Catalin Ltd., 54 Farm Hill Road, Waltham Abbey, Essex, England.
Cathodeon Ltd., Church Street, Cambridge, England.
Chance Bros. Ltd., Lighthouse Works, Smethwick 40, Birmingham, England.
Ciba (A.R.L.) Ltd., Duxford, Cambridge, England.
Corning Glass Works, 1946 Crystal Street, Corning, New York, U.S.A.
Cray Valley Products, Cray Valley, St. Mary Cray, Kent, England.
Creators Ltd., Silmay works, Kings Road, New Haw, Weybridge, Surrey, England.
Croid Ltd., Imperial House, 15–19 Kingsway, London, W.C.2, England.
Cynamid Products Ltd., Brettenham House, Lancaster Place, London, W.C.2, England.
Dalton Ballard and Co., Ltd., Fleet Place, Upper Park Road, London, N.W.3, England (Suppliers of 'Sindanyo').
Dow Corning Corp., Midland, Michigan, U.S.A. (Silicone products).
Dunlop Rubber Co., St. James's House, St. James's Street, London, S.W.1, England.
Enthoven Solders Ltd., Upper Ordnance Wharf, Rotherhithe Street, London, S.E.16, England.
Ferguson Edwards, The Maltings, Abbey Road, Barking, Essex, England.
Flexibox Ltd., Mechanical Seals, 76, Jermyn Street, London, S.W.1, England.
Fry's Metal Foundries Ltd., Tandem Works, Merton Abbey, London, S.W.19, England.

Garlock Packing Co., Palmyra, New York, U.S.A.
Geigy Ltd., 46, Old Bond Street, London, W.C.1, England.
General Electric Co., Ltd., Magnet House, Kingsway, London, W.C.2, England.
Griffiths Bros., Marks Road, London, S.E.16, England.
Hardman and Holden, Manox House, Canal Street, Manchester 10, England.
Hulburd Patents Ltd., 26, Park Road North, London, W.3, England.
Imperial Chemical Industries Ltd., Paints Division, Wexham Road, Slough, Bucks., England.
Imperial Chemical Industries Ltd., Plastics Division, Black Fan Road, Welwyn Garden City, Herts., England.
Jenaer Glaswerke, Schott und Gen., 10, Hattenbergstrasse, Mainz, West Germany.
Johnson and Matthey Ltd., 78–83, Hatton Garden, London, E.C.1, England.
Knapsack-Griesheim A.G., Knapsack near Cologne, Germany.
Kulite Tungsten Co., Ridgefield, New Jersey, U.S.A.
Libbey-Owens-Ford Glass Co., 608, Madison Avenue, Toledo 3, Ohio, U.S.A.
Linde's Eismaschinen A.G., 76, Nymphenburgerstrasse, Munich 2, Germany.
Marinite Ltd., 25 and 27, North Row, London, W.1, England.
Megatron Ltd., 105A, Fonthill Road, London, N.4, England.
Metallwerk Plansee, Reutte, Tirol, Austria.
Midland Silicones Ltd., 19, Upper Brook Street, London, W.1, England.
Mond Nickel Co., Ltd., Thames House, Millbank, London, S.W.1, England.
Morgan Crucible Co., Ltd., Battersea Works, Battersea Church Road, London, S.W.11, England.
Murex Ltd., Rainham, Essex, England.
Nu-Finishes Ltd., 466, London Road, Croydon, Surrey, England.
Perdeck Solder Products Ltd., Abbey Mills, Waltham Abbey, Essex, England.
Phenogeaze Ltd., 466, London Road, Croydon, Surrey, England.
Plowden and Thompson Ltd., Stourbridge, Worcester, England.
Powell Duffryn Carbon Products Ltd., Springfield Road, Hayes, Middx, England.
Precision Rubbers Ltd., Bagworth, Leics., England.
Redifon Ltd., Broomhill Road, London, S.W.18, England.
The Sheffield Smelting Co., Ltd., Royds Mill Street, Sheffield 4, Yorks., England.
Shell Chemical Co., Ltd., Norman House, 105–9, Strand, London, W.C.2, England.
Steatite and Porcelain Products Ltd., Stourport-on-Severn, Worcestershire, England.
Sylvania Electric Products Inc., 1740, Broadway, New York 19, U.S.A.
Thermal Syndicate Ltd., 9, Berkeley Street, London, W.1, England.
Thornley and Knight Ltd., Green Road, Bordesley, Birmingham 9, England.
Telefunken G.m.b.H., 100, Söflingerstrasse, Ulm/Donau, West Germany.

Tungsten Manufacturing Co., 68, Victoria Street, London, S.W.1, England.
Vactite Ltd., 75, St. Sinion St., Salford 3, Lancs., England.
G. and I. Weir Ltd., Cathcart, Glasgow, S.4, Scotland.
Westinghouse Electric Corp., East Pittsburgh, Pennsylvania, U.S.A.
Winslow Engineering Co., Newark, New Jersey, U.S.A.

OTHER ORGANIZATIONS REFERRED TO IN THE TEXT

Aluminium Development Association, 33, Grosvenor Street, London, W.1, England.
American Vacuum Society Inc., Box 1282, Boston 9, Massachusetts, U.S.A.
British Standards Institution, British Standards House, 2, Park Street, London, W.1, England.
International Organization for Vacuum Science and Technology, 30, Avenue de la Renaissance, Brussels, Belgium.
Tin Research Institute (Enquiries), 8, Spenser Street, London, S.W.1, England.

JOURNALS CONCERNED PRIMARILY WITH VACUUM TECHNOLOGY ARE:

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Vacuum, published by Pergamon Press, Headington Hill Hall, Oxford, England.
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